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DEVELOPMENT OF TECHNOLOGY FOR PRODUCTION, SAMPLING AND ASSAY OF SIMULATED ATMOSPHERES IN CLOSED CHAMBERS

Prepared for:

CHEMICAL CORPS RESEARCH AND DEVELOPMENT COMMAND
BIOLOGICAL WARFARE LABORATORIES, FORT DETRICK, FREDERICK, MARYLAND

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Final Report

DEVELOPMENT OF TECHNOLOGY FOR PRODUCTION, SAMPLING AND ASSAY OF SIMULATED ATMOSPHERES IN CLOSED CHAMBERS

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S R I Project No. SU-2285

Prepared for:

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DEVELOPMENT OF TECHNOLOGY FOR PRODUCTION, SAMPLING, AND ASSAY OF SIMULATED ATMOSPHERES IN CLOSED CHAMBERS

I INTRODUCTION

During 1956, Stanford Research Institute completed a project for Fort Detrick under Contract No. DA-18-064-404-CML-123, in which the literature relating to metropolitan air pollutant concentrations was reviewed and in which extensive tabulations were made of measured concentrations of pollutants found in metropolitan atmospheres in connection with air pollution investigations.[1] On the basis of these tabulations, a pollutant simulant mixture was selected which was considered representative of the maximum concentrations of components in metropolitan atmospheres. Techniques and equipment for production, sampling, and assay of the proposed test mixture in a test chamber were suggested.

The purpose of the investigations described in this report was to develop a method for producing the test atmosphere in an experimental chamber and for sampling and analyzing it, and to estimate the error associated with the assay of each of the constituents over a 2-hr period. A 1900-liter stainless steel chamber was used in these tests, but techniques were considered on the basis of scale-up to a chamber capacity of 1 million liters. Relative humidity in the chamber was maintained at 85%, with the exception of selected tests conducted to confirm the validity of techniques, in which the humidity of the test atmosphere was 40%. The atmosphere was stirred during each test.

The experimental work was conducted in 3 parts. In part I, optimum methods were investigated for producing, sampling, and analyzing the individual gases in the test atmosphere described in ref. (¹), and in Appendix A of this report. The applicability of the method was based upon experimental work in this program, a survey of the literature, and previous experience. The sampling and analysis methods were evaluated by the following criteria: (a) the method was to be sensitive in the required concentration range, (b) interferences from other constituents in the mixture were to be absent or determinable, (c) a minimum amount of test atmosphere was to be used for each analysis in order to prevent gross

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[1] Wohlers, H. C. and G. B. Bell. Literature review of metropolitan air pollutant concentrations--preparation, sampling, and assay of synthetic atmospheres. SRI Project No. SU-1816. Final Report, November 30, 1956.

dilution of the test atmosphere, (d) the simplest, most direct, and most rapid methods were to be used whenever possible, preferably wet-chemical methods, so that the monitoring system could be reproduced at other laboratories, and (e) methods were to be selected which could be performed in bacteriological safety cabinets, or in which the sample could be sterilized.

Appropriate injection, sampling, and analytical methods were tested for each gas in the test atmosphere, using the initial concentrations given in Appendix A. Single-constituent atmospheres of the following gases were monitored over 2-hr periods: acetaldehyde, acetic acid, acetylene, acrolein, ammonia, benzene, carbon monoxide, formaldehyde, hexane, hydrogen cyanide, hydrogen fluoride, hydrogen sulfide, nitrogen dioxide, ozone, sulfur dioxide, and sulfuric acid.

In part II, simulated atmospheres were prepared with all gases present, and individual gases were monitored over 2-hr periods in order (a) to test the efficiency of a special gas injection system which had been built to deliver mixtures of gases into the chamber, (b) to determine the applicability of the sampling and analytical methods when testing the complete gas mixture, and (c) to test for reactions between the gases.

The complete simulated atmosphere was tested in part III. A mixture of particulates was injected into the chamber along with the gases, and the concentrations of gases and aerosol were monitored.

An estimate of the experimental error associated with the sampling and analytical methods was made on each part of the program. The regression line for the log of concentration with time was obtained in each case, together with a test of the significance of the regression, and 95% confidence intervals for the true slope. In part II, 3 samples of a particular gas were obtained over the 2-hr period on each of 2 days selected at random, in order to test for day effects. The 6 values were then combined, disregarding day effects, and a new estimate of experimental error was obtained. Part III was similar to part II in respect to experimental design and treatment of data, except that 3 samples of a particular gas were collected on 3 separate days. The results from parts II and III were then combined (disregarding day effects) in order to obtain a higher degree of confidence in the results of the assay.

An estimate was made of the number of measurements of each gas in the mixture that would be required to determine the presence of a time trend during the 2-hr period, allowing in each case for an acceptable variation due to sampling and analysis.

Selected experiments were made at a relative humidity of 40% to check for gross effects of humidity on the complete test atmosphere.

Finally, the techniques were considered in respect to scaled-up chamber size and to the collection of samples in bacteriological safety cabinets.

II SUMMARY AND CONCLUSIONS

An appropriate sampling and analytical method was found for each of the gases when the single-constituent atmospheres were monitored in part I. The concentrations of acetaldehyde, acetic acid, carbon monoxide, formaldehyde, hydrogen fluoride, nitrogen dioxide, ozone, and sulfur dioxide decreased significantly* during the 2-hr test periods.

A method was developed for preparing the gas mixture in the chamber for part II of the program. Aldehydes in the mixture could not be determined separately due to interferences of the mixture with the analytical method. They were determined by another method as "total aldehyde." Hydrogen fluoride was omitted from the mixture because an excessive amount had to be injected into the chamber in order to obtain the required initial concentration. Sulfuric acid and acetic acid disappeared immediately from the complete mixture. They probably reacted with the ammonia, forming ammonium sulfate and acetate. Hydrocarbons could be identified only when the chamber relative humidity was 40%, due to the nature of the analytical technique. Carbon monoxide, nitrogen dioxide, ozone, and sulfur dioxide decreased significantly during the 2-hr periods. A day effect was present in the case of sulfur dioxide.

A better measure of significance was obtained in part III, in which the gases were monitored in the mixture of gases and particulates, than in part II, because each gas was tested on 3 days rather than on 2 days. Total aldehydes, nitrogen dioxide, ozone, and sulfur dioxide decreased significantly during the 2-hr periods. Day effects were present in the cases of total aldehydes and hydrogen cyanide.

The aerosol concentration was monitored during each 2-hr test in part III, using a smoke photometer. The total weight of aerosol injected for each test was 1.2 mg. Half of this quantity consisted of carbon black in the sub-micron range. The mean diameter of the other materials in the mixture was 1 μ. There was no significant decrease in the number concentration of particles in the chamber over the 2-hr test periods, indicating that a large amount of the material was in the sub-micron range, and did not settle out under the conditions of stirred settling. Tests were made to collect the settled material on glass slides, but no significant amount of material was collected because of the low initial concentration in the chamber.

A single test was made for each constituent in part III when the test mixture was at 40% RH. In each case the sample was drawn after the mixture had aged for 15 min. No gross effect of the lower humidity was observed.

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* The 5% confidence level was used in all significance tests throughout the program.

Although a complete program would be necessary to detect significant effects of humidity, no gross effects would be expected under these experimental conditions. (A significant effect of humidity was observed in the case of sulfuric acid in part I. However, the acid disappeared initially in the complete mixture, as previously mentioned.)

Time trends were shown to be present only in the cases of nitrogen dioxide, ozone, and sulfur dioxide when the results obtained in parts II and III were combined, ignoring day effects. An estimate was then made of the number of observations which would be required in order to monitor each gas, accepting slope variations equal to the variations obtained when the two parts were combined. Nine observations of each constituent would be required.

The methods of preparing the mixtures and monitoring the constituents described in this report are applicable to scale-up. It is suggested that the materials, even ozone, be allowed to decay naturally, although concentrations fall off rapidly to an undetectable level. The synthetic mixture treated in this manner would represent at least as good an "average" condition in nature as a constant concentration would, because there are wide variations in the concentrations of these pollutants in outside atmospheres, and because the test atmosphere represents a high average concentration of these pollutants. In addition, if make-up techniques were used, the results obtained on this project would not necessarily apply.

Finally, suggestions are given for monitoring the constituents under bacteriologically safe conditions.

III EXPERIMENTAL PROCEDURES

A. Description of Test Chamber

The test chamber was constructed by the Rheem Manufacturing Company.* It is shown in Figure 1. It had a capacity of 1800 liters, and was made of type 302 stainless steel, welded throughout. It had a dished head and bottom with a 16-in.-diameter manhole in the front, and a Lucite manhole cover. All fittings, including the manhole, were flush with the inside of the tank. The test atmosphere in the chamber was stirred by 2 fan blades 36 in. in length and pitched to 30 degrees, located in the lower part of the chamber. There was a clearance of 6 in. between the blades and the chamber wall. The shaft of the fan extended through a packing seal in the bottom of the chamber, and was driven by a Boston ratio motor fastened to the floor. The shaft speed was 86 rpm, and the tip speed was 13.5 ft/sec. A 100-cfm blower with a magnetic valve was attached to the top center of the chamber, and was used to flush out the chamber between tests. A 3-in.-diameter stainless steel pipe extended from the lower part of the chamber to above the roof of the building. Fresh, outside air entered this tube to replace the air drawn out of the chamber when sampling. A relative humidity very close to 85% was maintained in the chamber during a test by means of a soaked sponge located in the air inlet tube.** A wet and dry bulb hygrometer was attached to the transparent manhole cover. The wet bulb of the hygrometer was kept moist by adding water through a small hole in the manhole. The hole was stoppered when not in use. A drain was fastened to the base of the chamber for cleaning purposes. The front of the chamber had 5 ports. Ports not in use were covered with screw caps.

A determination was made of the mixing efficiency in the chamber. For these tests, glycerine aerosol was prepared with an atomizer-type generator. The generator delivered particles with an average diameter of 1 μ at a rate of 10 mg aerosol/min. The aerosol was introduced into the chamber in the same manner in which the test gases were introduced (described in the following section) until the glycerine concentration in the chamber was 0.5 γ/liter to 1.2 γ/liter. The aerosol was then drawn through a Sinclair-Phoenix forward scattering smoke photometer from 5 locations in the chamber, and the mixing characteristics under test conditions were determined in terms of the relative aerosol concentration at a particular location and at a particular time. The time for complete mixing at a port was taken as the time that a rise in concentration was completed, and decay had begun. The 5 ports were tested in random order.

* Rheem Manufacturing Company, 801 Chelsey, Richmond 4, California.

** Relative humidity of fresh air in the San Francisco Bay Area is usually between 30% and 60%.

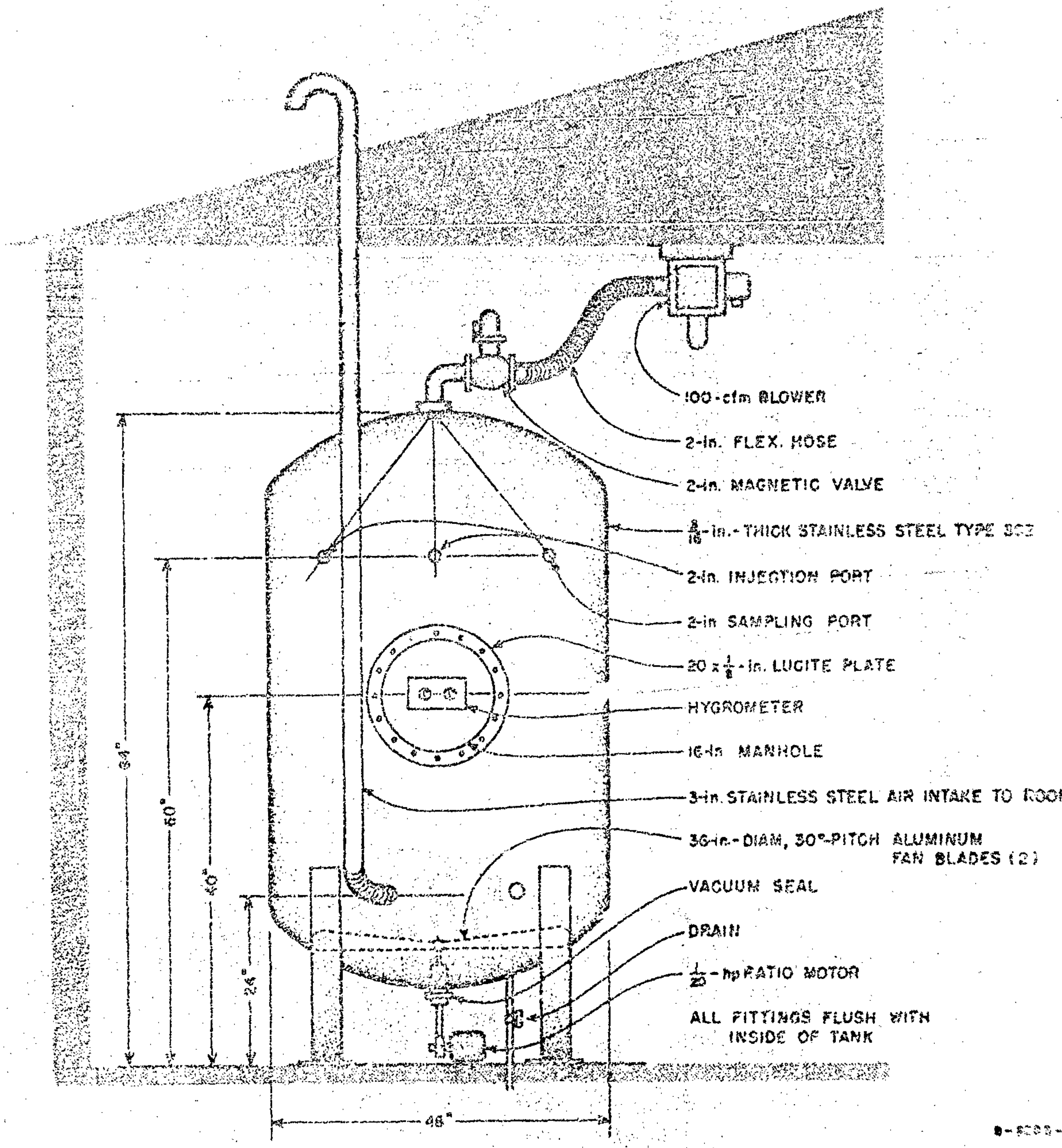

FIG. 1

TEST CHAMBER

TABLE I

MIXING EFFICIENCY IN CHAMBER

Glycerine Particles, Average Diameter 1 μ

TEST NO	SUCCESSIVE SAMPLING POINTS*	AMOUNT OF GLYCERINE ADDED TO CHAMBER, γ/liter	$\Delta c/c_0$**	TIME FOR COMPLETE MIXING, sec
1	1 2 1 2 1	1.2	+ 8% 0 0 - 7% 0	25
2	2 3 2 3 1 5 1	1.2	0 0 0 0 0 0 0	7
3	4 2 4 2 3	1.2	0 + 3% 0 0 0	20
4	5 2 5	0.5	0 + 8% 0	20
5	5 3 5	1.2	0 +10% 0	20

* Locations of sampling points were as follows: No. 1 was at the sampling level (2/3 the tank height), and 10 in. from the right wall, facing the tank. No. 2 was at a position 1/3 the tank height, below No. 1, and 1 in. from the front wall. No. 3 was 1 in. above the bottom center, below the fan. No. 4 was about 6 in. down from the top center. No. 5 was at the same port as No. 2, but the sampling point was 10 in. from the opposite wall.

** Where C_0 is the average concentration-decay line. Instrument variation ±10%.

The results are given in Table I. A maximum of 25 sec was required for complete mixing as measured by this method.

Tests of different methods of cleaning the chamber between runs were made during part I of the program. The most satisfactory method was to flush the chamber overnight by drawing outside air through it by means of the 100-cfm blower.

B. Injection Procedure

1. Gas Injection

Four methods were used to inject the test gases into the chamber: (1) nitrogen dioxide, ammonia, sulfur dioxide, hydrogen sulfide, carbon monoxide, and acetylene were supplied from gas cylinders and were swept into the chamber in a stream of nitrogen; (2) ozone and hydrogen cyanide were generated outside the chamber, and were swept into it in the nitrogen stream; (3) formaldehyde, acetaldehyde, acrolein, benzene, hexane, acetic acid, and sulfuric acid were evaporated into the chamber; and (4) hydrogen

fluoride was introduced by bubbling air through a solution of hydrogen fluoride. Hydrogen fluoride was injected only in part I, as noted previously.

a. Injection of Cylinder Gases

The equipment used to inject cylinder gases and generated gases into the test chamber is shown in Figure 2. The equipment was mounted on a cart, and during operation was connected to the center injection port above the manhole, shown in Figure 1. Gases were delivered from the port into the center of the chamber through a 2-ft glass tube. All stopcocks were turned to a closed position after the injecting system was connected to the chamber. Line air, 10 liters/min, was allowed to flow through the exhaust manifold. The nitrogen was then turned on, and the solenoid valve was opened. The nitrogen flow into the chamber was adjusted to 10 iters/min, a reading of 8 on the rotameter scale. The sweep-gas system was equipped with an automatic timer to the solenoid valve, but the timer was not used.

Acetylene, 0.55 ppm,* was injected first. The stopcock in the acetylene line was opened to the exhaust manifold, and the cylinder valve was cracked for 30 sec. The acetylene syringe was opened to 1.2 cc.** The acetylene was turned off, the stopcock was turned to the sweep manifold, and the acetylene in the syringe was injected into the gas stream entering the chamber. The acetylene stopcock was then turned to an off position.

The stopcock in the carbon monoxide line was opened to the exhaust manifold, during the 30 sec flushing with acetylene described above, and the carbon monoxide cylinder needle valve was opened until the rotameter reading was 7.5. This indicated a flow of 40 cc/min. After completion of the acetylene injection, the stopcock in the carbon monoxide line was turned to the sweep manifold for 30 sec, which allowed 20 cc (10 ppm) of the gas to be swept into the tank. The cylinder valve was closed at the end of the 30-sec period, and the stopcock was turned to the off position.

Ammonia was added next. The stopcock was opened to the exhaust manifold, and the cylinder valve was cracked. The syringe was opened to 0.72 ml. After 30-sec flushing, the gas was turned off, and the stopcock was turned to the sweep manifold. The gas in the syringe was injected into the sweep manifold, and the stopcock was turned off.

Sulfur dioxide, hydrogen sulfide, and nitrogen dioxide were added in quick succession in the same manner as the ammonia. They were

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* Parts per million by volume are given throughout the report unless otherwise noted.

** About 20% excess of the required gas volumes were metered in the syringes to allow for losses due primarily to the gas residue remaining in the fine-bore tubing extending from the stopcocks to the sweep-gas manifold.

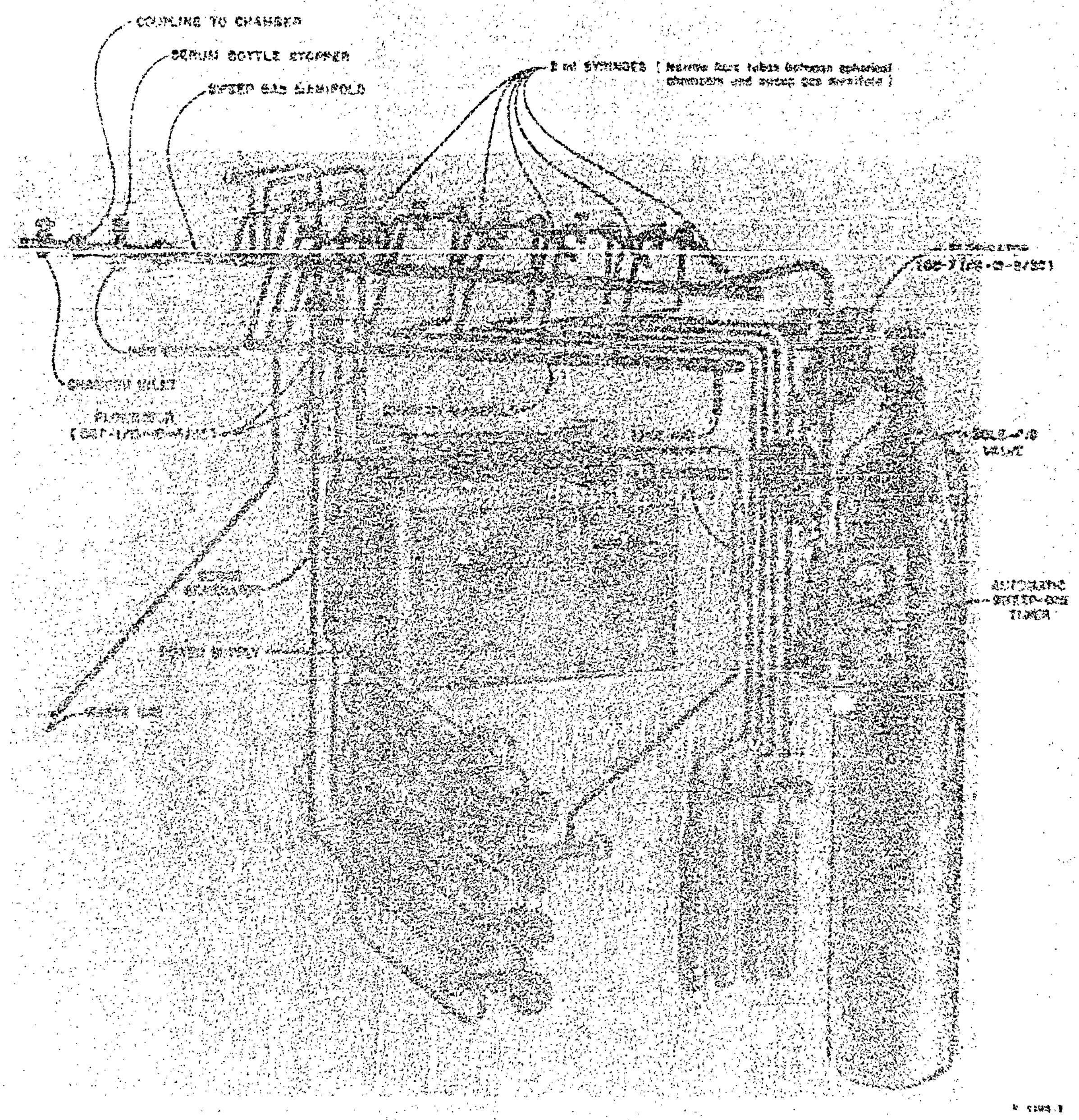

FIG. 2

INJECTION SYSTEM FOR CYLINDER GAS AND GENERATED GAS

turned on and allowed to flush into the exhaust manifold during the 30-sec flushing period for the ammonia. The syringes were adjusted to deliver the following amounts: sulfur dioxide, 12 cc (5 ppm delivered),* hydrogen sulfide, 0.48 cc (0.2 ppm delivered), and nitrogen dioxide, 2.4 cc (1.0 ppm delivered).

b. Injection of Generated Gases

Hydrogen cyanide and ozone were added next. Hydrogen cyanide, 0.15 ppm, was introduced in the following manner. Potassium cyanide, 0.80 mg, was placed in the hydrogen cyanide generator shown in Figure 2. One-half ml of 50% sulfuric acid was added through the serum stopper of the generator, and the hydrogen cyanide which was produced was swept into the tank with the nitrogen stream.

The power supply for the ozone generator was turned on and adjusted to 64V during the preceding operations to allow about 2 min warm-up. The stopcock in the oxygen line was opened to the exhaust manifold, the oxygen cylinder valve was cracked, and the oxygen flow was adjusted to 15.6 on the rotameter (2 liters/min). The stopcock was then opened to the injection manifold, and gas was allowed to flow from the ozonizing tube into the chamber for 3 min, 18 sec. It had been determined by previous calibration that 2.0 ppm ozone were present at the end of the injection period under these conditions. The ozonizer was calibrated at intervals throughout the program, and the length of time of flow into the chamber was changed accordingly.

c. Injection of Evaporated Gases

The remainder of the gases, and the sulfuric acid aerosol, were evaporated into the chamber while the ozone was being added. Acetic acid, benzene, n-hexane, formaldehyde, acetaldehyde, and acrolein were evaporated from a 10-ml crucible. A heating element consisting of #24 nichrome wire was wound around the crucible, and was covered with #27 heat-resistant Scotch electrical tape. The heating element extended to a 105V variac. A copper-constantan thermocouple extended from the bottom of the crucible to a microammeter. The crucible was fastened on a 20-in. rod. After the required amounts of materials had been added, the crucible was inserted into the chamber through the left-side upper port, extending 18 in. inside the chamber. The variac was then turned to 12V until a sudden swing of the ammeter indicated that the crucible was dry. The following amounts of the liquids were evaporated from the crucible:

* In practice, the sulfur dioxide was added from a 20-cc syringe through a serum bottle stopper shown in Figure 2, because the mounted syringe was too small. It had not been anticipated that such a large amount of the gas would be necessary.

A stock solution of 10 g acetic acid in 1000 ml water was prepared, and 0.1 ml was added to the crucible. This represented 1 mg of the acid, which on evaporation yielded the required 0.2 ppm in the chamber.

A liter of stock solution containing 0.740 g formaldehyde, 0.360 g acetaldehyde, and 0.920 g acrolein in water was prepared. One ml of this solution was also added to the crucible, representing 0.7 mg formaldehyde, 0.36 mg acetaldehyde, and 0.920 mg acrolein. On evaporation, the required 0.30 ppm of the formaldehyde, and 0.10 ppm each of acetaldehyde and acrolein, were evaporated into the chamber.

Benzene, 0.17 mg, and n-hexane, 2.0 mg, were added to the crucible with micropipettes. This represented the required 0.27 ppm of benzene and 0.28 ppm hexane after evaporation into the chamber.

Sulfuric acid has a boiling point of over 300°C, and was evaporated into the chamber in a different manner. A stock solution containing 1.85 ml sulfuric acid/liter was prepared. One-tenth ml of this solution was transferred to a 6-in. spiral of alloy K, 1.3 Ω/ft, resistance wire. The wire extended to a 6.3V filament transformer, which was supplied by 105V from a variac. It was fastened on a 20-in. rod, and after charging with the acid was fastened in the chamber in the same manner as the crucible. The wire turned cherry red (~650°C) when heated, and the sulfuric acid vaporized within 30 sec as a puff of white smoke. Sulfuric acid has an extremely low vapor pressure at room temperature, and exists as droplets in polluted atmospheres. The 0.1 ml solution which was evaporated represented 0.340 mg in the chamber, or 0.05 ppm by volume (0.14 ppm by weight).

d. Injection of Hydrogen Fluoride

The method of introducing hydrogen fluoride in part I of the project was a follows. Air was bubbled at a rate of 10 liters/min through a 10% aqueous solution of hydrogen fluoride held at 0°C in an ice bath. Under these conditions the gas stream entering the chamber contained 66 γ/liter (80 ppm) of hydrogen fluoride.* It was necessary to add hydrogen fluoride over a 57-min period before the required concentration of 0.0072 ppm was obtained in the test chamber.

2. Aerosol Injection

The dust mixture which was injected along with the gases in part III consisted of 30 chemicals, ground separately in a Beckman/Spinco Spinmill,** and carbon black. An oil aerosol was injected by means of a liquid aerosol

* Calibration of the hydrogen fluoride gas stream was prepared for another project by Dr. Moyer D. Thomas of these laboratories.

** The grinding was carried out at Spinco Division, Beckman Instruments, Inc., 1117 California Avenue, Palo Alto, California. The Spinmill was operated under the supervision of Mr. William Oats, Engineer, and Mr. Whitelaw Wright, Product Line Supervisor, both of Spinco.

dispenser,[2] and Figure 3, at the same time that the dust mixture was injected. Measurements were taken of the particle size distributions of the chemicals, both before and after grinding. Size distributions of the separate materials are given in Table II. Two hundred particles of each material were measured with an optical microscope. All the materials except copper sulfate were ground to a median diameter between 0.4 μ and 2.1 μ. The ground chemicals were then mixed in proportions which are typical of those found in polluted atmospheres. The weight percent of each of the chemicals in the dust mixture is given in Table III, together with the weight of each material introduced into the chamber in an experiment. Carbon black comprised about half the weight of material injected. It was not present in the stock mixture. A working mixture was prepared for the tests which included the carbon black. The cumulative size and weight distributions of the particles in the stock dust mixture are given in Table IV. Eight hundred particles were measured. Fifty percent of the particles were less than 1.0 μ in diameter, and 50% of the mass was present in particles less than 2.5 μ in diameter. The count does not include particles less than about 0.5 μ, the lower limit of resolution of the microscope. Both on a number basis and on a weight basis the effect of these particles in a test would be small in proportion to an effect contributed by the carbon black, which has a median diameter of 0.025 μ, determined by electron micrography.

The dust to be injected into the chamber, 1.1 mg in each test, was contained in small gelatine capsules, and was injected into the chamber through an upper port by means of a Benjamin air pistol. The capsule fragments fell out very rapidly, and the aerosol was dispersed throughout the chamber in seconds, as described in the following section.

Used crankcase oil was used for the oil aerosol. The aerosol was injected into the chamber by means of a calibrated dispenser as shown in Figure 3. Under 5 lb pressure, the dispenser delivered the required 60 micrograms of oil in 10 sec. The oil particles were 1 to 5 μ in diameter.

The total time required to inject all the materials into the chamber varied between 3 and 5 min, depending primarily on the calibration of the ozone generator.

C. Methods of Assaying Constituents

1. Methods of Sampling and Analysis

All methods of sampling and analyzing the gases which were tested on the program are described in Appendix A, together with a brief discussion of each method and its applicability to other monitoring programs. The hydrocarbons were determined in parts I and II with an automatic instrument,

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[2] Cadle, R. D., and P. L. Magill. Preparation of Solid- and Liquid-in-Air Suspensions. Ind. Eng. Chem., 43, 1331-1335, June, 1951.

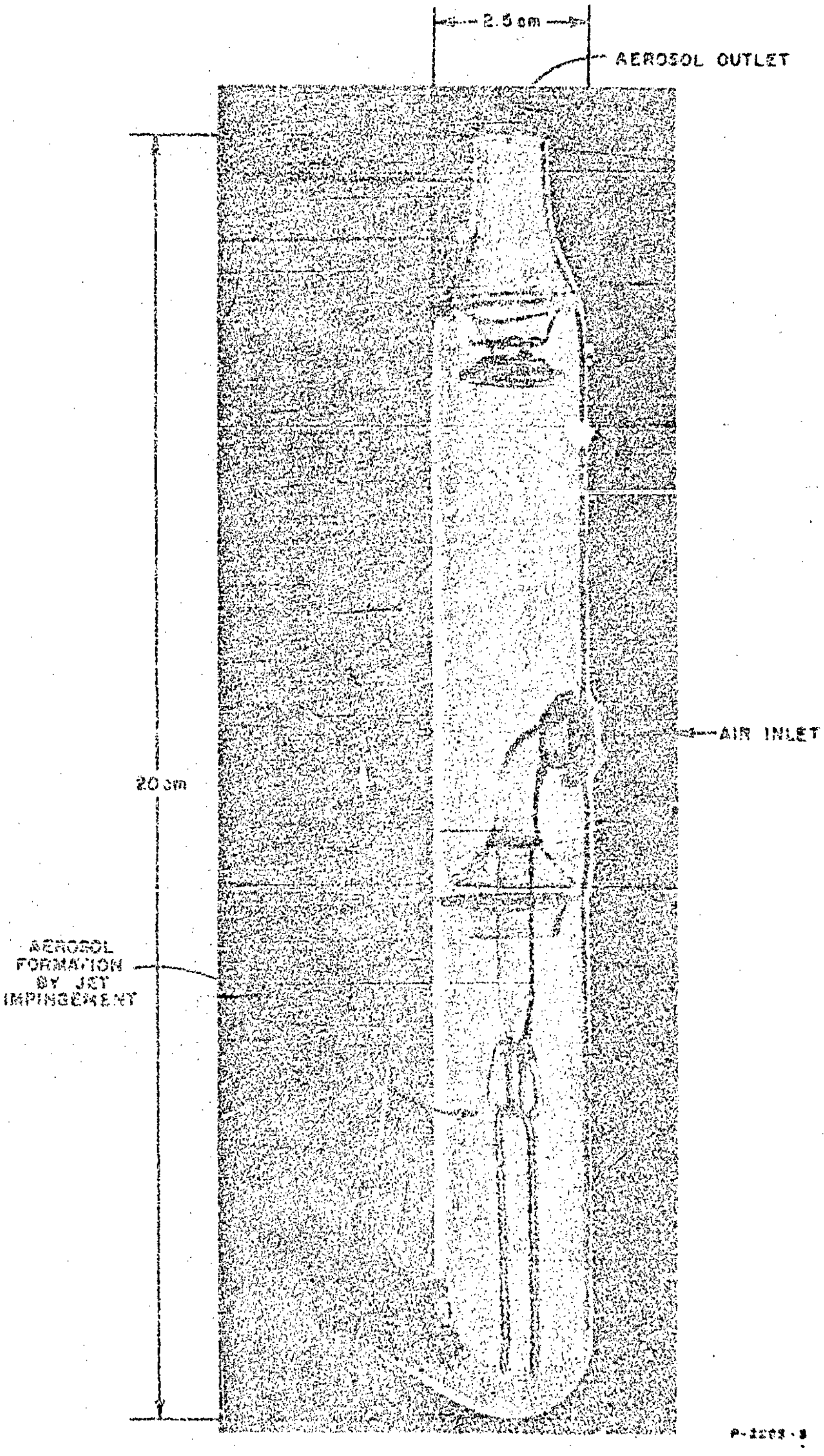

FIG. 3
CALIBRATED OIL AEROSOL DISPENSER

TABLE II

SIZE DISTRIBUTIONS OF MATERIALS USED IN DUST MIXTURE
BEFORE AND AFTER GRINDING IN BECKMAN/SPINCO "SPINMILL"

MATERIAL*	BEFORE GRINDING**		AFTER GRINDING**	
	Percent of particles less than 1 μ diameter	Number Median diameter, μ	Percent of particles less than 1 μ diameter	Number Median diameter, μ
Aluminum potas. sulfate	5	10.0	23	1.6
Antimony trioxide	31	1.1	68	0.8
Arsenious acid	7	3.2	13	2.0
Bismuth oxide	2	2.5	53	1.0
Cadmium oxide	37	1.3	80	0.6
Calcium carbonate	<1	6.0	22	1.8
Calcium fluoride	6	3.3	40	1.2
Calcium sulfate	30	3.2	86	0.6
Calcium tungstate	24	2.5	60	0.9
Carbon black	100	0.025	not ground	
Chromium oxide	10	1.5	80	0.6
Cobalt oxide	2	5.5	80	0.6
Copper sulfate	12	50.0	14	19.0
Ferric oxide	73	0.8	93	0.4
Imperial clay	70	0.4	74	0.5
Lead monoxide	4	2.2	71	0.7
Lead sulfate	18	1.5	42	1.1
Lithopone	18	2.2	20	1.9
Magnesium sulfate	10	3.8	92	0.6
Manganese dioxide	20	1.6	20	1.7
Mercury chloride	<1	2.8	20	2.0
Molybdic acid	10	20.0	27	1.5
North Carolina feldspar	2	10.0	36	1.2
Potassium sulfate	21	2.1	17	2.1
Sodium nitrate	15	3.5	20	2.0
Sodium sulfate	13	2.0	18	2.0
Stannous oxide	2	23.0	64	0.8
Titanium oxide	92	0.3	95	0.6
Vanadium pentoxide	3	3.0	67	0.8
Zinc oxide	50	1.0	88	0.5
Zinc sulfide	30	2.1	11	2.1

* Coarse materials hand-ground in mortar before machine grinding.

** Cumulative size distributions of individual materials may be obtained by plotting the 2 points as log of the diameter against percentage of particles less than indicated diameter, using log probability paper. A straight line can then be drawn through the 2 points to include 2% to 98% of the size distribution.

TABLE III

COMPOSITION OF TEST DUST MIXTURE

MATERIAL	WEIGHT % IN STOCK DUST SAMPLE	WEIGHT INJECTED INTO CHAMBER, γ/2 cu m
Aluminum potas. sulfate	6.100	34.00
Antimony trioxide	0.258	1.44
Arsenious acid	0.025	0.14
Bismuth oxide	0.036	0.20
Cadium oxide	0.021	0.12
Calcium carbonate	0.500	2.80
Calcium fluoride	0.214	1.20
Calcium sulfate	20.000	111.60
Calcium tungstate	0.169	0.94
Carbon black*		600.00
Chromium oxide	0.007	0.04
Cobalt oxide	0.007	0.04
Copper sulfate	1.395	7.80
Ferric oxide	5.140	28.60
Imperial clay	14.800	81.80
Lead monoxide	1.140	6.40
Lead sulfate	0.750	4.20
Lithopone	0.143	0.80
Magnesium sulfate	14.300	80.00
Manganese dioxide	0.032	0.18
Mercuric chloride	0.100	0.56
Molybdic acid	0.053	0.30
North Carolina feldspar	12.500	70.20
Potassium sulfate	6.850	38.20
Sodium nitrate	7.070	39.48
Sodium sulfate	7.200	40.20
Stannous oxide	0.057	0.32
Titanium oxide	0.053	0.30
Vanadium pentoxide	0.057	0.32
Zinc oxide	0.895	5.00
Zinc sulfide	0.128	0.78
Total Dust	100.000	1157.94
Oil aerosol**		60.00
Total Weight of Test Aerosol		1217.94 micrograms

* Not present in stock mixture. Present in working mixture.

** Added to tank by means of liquid aerosol dispenser.

TABLE IV

SIZE DISTRIBUTION OF PARTICLES IN DUST MIXTURE

PARTICLE DIAMETER, μ	CUMULATIVE DISTRIBUTION OF PARTICLE DIAMETERS, % (measured)	CUMULATIVE DISTRIBUTION OF PARTICLE WEIGHT, % (calculated*)
less than 1.0	50	4
less than 1.5	76	16
less than 2.0	91	32
less than 2.5	95	49
less than 3.0	98	62
less than 5.0	99	90
less than 6.0	99.9	95

* Calculated from the following relationship of geometric mean diameter by weight with geometric mean diameter by count: $\log M_g = \log M_g' - 6.9078 \log^2 \sigma_g$, where M_g and M_g' are the geometric means by count and by weight respectively, and σ_g is the standard geometric deviation by count or by weight, i.e., the ratio of the 84.13% size to the 50% size. (Hatch, T. Determination of "average particle size" from the screen analysis of non-uniform particulate substances, J. Franklin Institute, 215, 27 (1933).)

using a Perkin-Elmer Model 12-C Infrared Spectrometer. Acetaldehyde and acrolein were determined polarographically on part I, but there were interferences when the method was applied to the mixture of gases. In parts II and III, total aldehydes as "formaldehyde" were determined by a titrimetric method. An automatic instrument was available for monitoring nitrogen dioxide,[3] and it was used to monitor the atmosphere during all tests in part II. However, the instrument was designed to monitor atmospheres with concentrations of oxides of nitrogen which were orders-of-magnitude less than those obtained on this program. It was therefore necessary to dilute the test air going into the instrument. It was difficult to maintain this dilution constant for 2-hr periods, and wide fluctuations developed which were inconsistent with previous experience in monitoring oxides of nitrogen with the instrument, and the measurements were not valid. A chemical method was subsequently used to monitor the nitrogen dioxide on two extra test days in part II, and three extra test days in part III. The single run for the determination of hydrogen fluoride was monitored with an automatic instrument, based on the selective quenching of the fluorescence of magnesium oximate by fluoride ion.[4] A wet chemical method, requiring 1 cfm of sample through the bubbler for 1 hr, is described in Appendix B. Except for the instrumental methods mentioned above, all tests were made manually, using standard wet chemical techniques.

Bubblers and impingers were used to collect samples for the determination of acetic acid, total aldehydes, ammonia, hydrogen cyanide, hydrogen sulfide, nitrogen dioxide, ozone, and sulfur dioxide. Carbon

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[3] Thomas, M. D., J. A. MacLeod, R. C. Robbins, R. C. Goettelman, and R. W. Eldridge, Automatic Apparatus for Determination of Nitric Oxide and Nitrogen Dioxide in the Atmosphere. Anal. Chem. 28, 1810, Dec., 1956.

[4] Chaikin, S. W., C. E. Glassbrook, and T. D. Parks. Paper presented at 123rd meeting, American Chemical Society, Los Angeles, California, March, 1953.

monoxide was collected and read directly in an indicating gel. Sulfuric acid droplets were collected on a Millipore filter, and were determined by titration. Sampling rates ranged from 0.6 liters/min to 10 liters/min, and the time to collect a sample ranged from 2 min to 30 min, depending on the sensitivity of the particular analytical procedure.

The concentration of particulate material in the chamber was monitored with a Sinclair-Phoenix Aerosol, Dust, and Smoke Photometer.* The instrument measured the forward scattering of light at small angles, and had a range which was sufficient to include the particulate concentrations used on this program. The aerosol concentration of each test in part III was monitored with this instrument, using a flowrate of 4.2 liters/min through the photometer, and an Esterline-Angus recorder to record the relative concentrations.

2. Corrections for Dilution in Chamber Due to Sampling

In all tests, it was necessary to correct the measured concentration of a constituent for the dilution in the chamber due to sampling up to the time that the particular sample had been collected. In part II, two gases were determined over a 2-hr period and 3 samples were collected for the analysis of each gas. (This experimental design was used to determine day effects, and is described in the next section of the report.) In addition to the dilution due to sampling the two gases, there was an additional dilution due to continuous sampling for nitrogen dioxide with the automatic apparatus. The dilution during each test in part III was similar to that in part II, except that the particulate material was also sampled continuously. Derivations of the equations which describe the dilution process, and an example of the calculations made in each part of the program are given in Appendix C.

D. Experimental Design

Part I of the study was considered to be primarily an evaluation of appropriate sampling and analytical techniques, and was concluded when sampling and analytical methods had been tested.

Part II, which was considered to be an exploratory stage leading to the studies of the mixture of gases and dust, was designed so that the variability due to days as well as to experimental error could be estimated.** Two gases were tested each day, and 3 samples of each gas were collected in the 2-hr period. Samples of the 2 gases were collected alternately. Each component was tested on two days, e.g., a particular gas was sampled

* Phoenix Precision Instrument Company, 3803-05 North Fifth Street, Philadelphia 40, Pennsylvania.

** Dr. Edwin L. Cox, Statistician at Fort Detrick, and Dr. Gerald Lieberman, Associate Professor of Statistics at Stanford University, designed the statistical program for parts II and III of the project.

at times 1, 3, and 5 on one day, and at times 2, 4, and 6 on another. The days on which the gases were sampled were chosen at random. In each case, the regression line and the 95% confidence interval for the true slope was determined.

Part III was designed in the same manner as part II, except that each gas was tested on three days, and the aerosol concentration was monitored continuously. The variability of the results proved to be too great on both parts II and III to permit distinguishing any effects of the aerosol on the gases in the mixture, and the two parts were combined in order to obtain a better estimate of the experimental error. Day effects were infrequent, and were ignored in combining the observations. These final determinations of the regression lines, and the corresponding 95% confidence intervals for the true slopes, were obtained from 15 observations for each gas. An estimate was then made of the number of observations which would be necessary when monitoring each gas in order to obtain results similar to those obtained with 15 observations, under these conditions, at the 95% confidence level. In order to make this estimate, a slope variation was accepted which was equal to the variation obtained when the 15 observations were combined. A description of the statistical treatment of the data is given in Appendix D.

IV RESULTS AND DISCUSSION

A. Results of Monitoring Atmospheres Containing a Single Test Gas

The concentrations of test atmospheres containing the required concentrations of a single test gas, obtained in part I of the program, are given in Table V.

It was found necessary to add excesses of ammonia, hydrogen fluoride, ozone, sulfur dioxide, and sulfuric acid in order to obtain the required initial concentrations in the chamber. Tests for acetylene and benzene plus hexane were made at a chamber humidity of 40% in order to avoid water interferences in the infrared spectrometer. The tests for hydrogen fluoride were also run at 40% humidity, due to interferences of water vapor with the automatic instrument. All other tests were made at 85% humidity.

The regression lines and 95% confidence intervals for the true slopes which were determined from these data are given in Table VI. Mid-points of sampling time were used for the calculations. Significant time trends were present in the tests of acetaldehyde, acetic acid, carbon monoxide, formaldehyde, hydrogen fluoride, nitrogen dioxide, ozone, and sulfur dioxide.

B. Results of Monitoring Atmospheres Containing the Mixture of Gases

Three tests of each gas were made on two separate days when testing the mixture of all the gases, as mentioned previously. Twelve days were required to make the determinations. The results are given in Table VII.

The regression lines, presence of day effects, and 95% confidence intervals for the true slopes which were determined from these data are given in Table VIII, using mid-points of sampling time. Acetic acid and sulfuric acid were absent. They were probably converted to ammonium acetate and sulfate respectively. Again, the hydrocarbons acetylene, benzene, and hexane were run at 40% humidity. All other tests were at 85% humidity. Day effects were present only in the tests of sulfur dioxide. Significant time trends were present in the tests of carbon monoxide, nitrogen dioxide, ozone, and sulfur dioxide when the 6 tests obtained on the two days were combined, ignoring day effects.

C. Results of Monitoring Atmospheres Containing the Mixture of Gases and Particulate Material

Three tests of each gas were made on three separate days when testing the mixture of gases and particulates in part III, and the concentration of particulates was monitored continuously during each test, using the Sinclair-Phoenix smoke photometer described previously. The concentrations of the test gases are given in Table IX. Acetylene, benzene, and hexane

TABLE V

CONCENTRATIONS OBTAINED IN TEST CHAMBER WHEN TESTING ATMOSPHERES CONTAINING A SINGLE GAS

GAS	AMOUNT INTRODUCED INTO CHAMBER, ppm by vol	SAMPLING TIME, min	CONCENTRATION, ppm by vol
Acetaldehyde	0.10 (0.18 γ/liter)	0-20	0.086
		25-45	0.081
		50-70	0.075
		75-95	0.075
		100-120	0.068
Acetic acid	0.40 (1.00 γ/liter)	0-15	0.40
		20-35	0.25
		45-60	0.10
		80-95	0.10
		110-125	0.08
Acetylene	0.55 (0.60 γ/liter)	0-2	0.55
		27-29	0.43
		95-97	0.72
		126-128	0.60
Acrolein	0.20 (0.46 γ/liter)	0-20	0.16
		25-45	0.15
		50-70	0.15
		75-95	0.19
		100-120	0.17
Ammonia	1.50 (1.08 γ/liter)	0-10	0.29
		20-30	0.34
		35-45	0.23
		82-92	0.31
		107-117	0.27
Benzene + Hexane	0.27 (0.85 γ/liter) benzene	0-2	0.55
		53-55	0.83
	0.28 (1.00 γ/liter) hexane	79-81	0.41
		101-103	0.51
		126-128	0.41
Carbon monoxide	10.0 (11.6 γ/liter)	0-5	10.0
		55-60	8.7
		115-120	7.5
		175-180	7.5
Formaldehyde	0.30 (0.37 γ/liter)	0-5	0.32
		20-25	0.28
		42-47	0.29
		52-57	0.28
		80-85	0.27
		100-105	0.20
		122-127	0.16
Hydrogen cyanide	0.15 (0.126 γ/liter)	0-20	0.14
		22-42	0.14
		44-64	0.14
		66-86	0.12
		110-130	0.17

TABLE V (*Concluded*)

GAS	AMOUNT INTRODUCED INTO CHAMBER, ppm by vol	SAMPLING TIME, min	CONCENTRATION, ppm by vol
Hydrogen fluoride	36.3 mg added (55 min of injection to obtain required "initial" concentration of 0.007 ppm, 0.0052 γ/liter)	0-5	0.0072
		5-10	0.0060
		10-15	0.0055
		15-20	0.0049
		22-27	0.0044
		28-33	0.0040
		37-42	0.0032
		45-50	0.0032
		55-60	0.0032
		65-70	0.0023
		80-85	0.0023
		92-97	0.0019
		105-110	0.0016
Hydrogen sulfide	0.20 (0.29 γ/liter)	0-30	0.25
		30-60	0.29
		90-120	0.24
		130-160	0.25
Nitrogen dioxide	1.00 (1.91 γ/liter) (tested with automatic analyzer)	0-10	1.04
		5-15	1.02
		15-25	0.94
		25-35	0.86
		35-45	0.85
		45-55	0.78
		55-65	0.69
		65-75	0.6[illegible]
		75-85	0.55
		85-95	0.51
		95-105	0.48
		105-115	0.48
Ozone	2.00 (3.9 γ/liter)	0-5	0.20
		10-15	0.12
		28-32	0.08
		45-50	0.06
		60-65	0.05
Sulfur dioxide	5.00 (13.2 γ/liter)	0-2	3.0
		9-11	2.4
		19-21	2.4
		40-42	1.4
		66-68	1.3
		117-119	0.5
		135-137	0.3
Sulfuric acid	0.41 (1.65 γ/liter)	0-10	0.07
		10-20	0.08
		30-40	0.05
		40-50	0.08
		60-70	0.06
		100-110	0.06

TABLE VI

SUMMARY OF RESULTS, PART I. SINGLE GAS IN CHAMBER

GAS	AMOUNT INTRODUCED, ppm	NO. OF SAMPLES	REGRESSION LINE $\log Y = b_0 + b_1x$	95% CONFIDENCE INTERVAL FOR TRUE SLOPE*
Acetaldehyde	0.10	5	$\log Y = -1.057 - 0.00094x$	−0.00130, −0.00058
Acetic acid	0.40	5	$\log Y = -0.459 - 0.0061x$	−0.0107, −0.0015
Acetylene	0.55	4	$\log Y = -0.30923 + 0.00097x$	+0.00387, −0.00183
Acrolein	0.20	5	$\log Y = -0.82417 + 0.00062x$	+0.00205, −0.00081
Ammonia	0.30	5	$\log Y = -0.53448 - 0.00018x$	+0.00244, −0.00208
Benzene + hexane	0.5[illegible]**	5	$\log Y = -0.10688 - 0.00129x$	+0.00476, −0.00228
Carbon monoxide	10.00	4	$\log Y = 0.98834 - 0.00074x$	−0.00134, −0.00014
Formaldehyde	0.30	7	$\log Y = -0.463 - 0.0023x$	−0.00337, −0.00103
Hydrogen cyanide	0.15	5	$\log Y = -0.88313 + 0.00056x$	+0.00238, −0.00126
Hydrogen fluoride	0.0072	13	$\log Y = -2.2009 - 0.00571x$	−0.00643, −0.00499
Hydrogen sulfide	0.20	4	$\log Y = -0.57089 - 0.00025x$	+0.00101, −0.00151
Nitrogen dioxide	1.00	12	$\log Y = 0.042 - 0.00347x$	−0.00381, −0.00313
Ozone	0.40	5	$\log Y = -0.7538 - 0.00948x$	−0.01362, −0.00534
Sulfur dioxide	5.00	7	$\log Y = 0.490 - 0.0070x$	−0.00832, −0.00568
Sulfuric acid	0.41	6	$\log Y = -1.1438 - 0.00085x$	+0.00178, −0.00348

* Regression was said to be present only if the confidence interval for the slope did not include zero.

** Equal quantities both hydrocarbons.

were added to the mixture, but were not monitored, because tests in parts I and II indicated that the infrared spectrometer underwent day-to-day variations, was relatively insensitive in this concentration range, and required a chamber humidity of 40% to remove water interferences.

The regression lines, presence of day effects, and 95% confidence intervals for the true slopes which were determined from these data are given in Table X, using mid-points of sampling time. The chamber humidity was 85% in all tests. Day effects were present in tests of total aldehyde and hydrogen cyanide. As expected, acetic acid and sulfuric acid disappeared.

Significant time trends were present in the tests of total aldehydes, nitrogen dioxide, ozone and sulfur dioxide when the 9 tests obtained on the 3 days were combined, ignoring day effects.

The results obtained when monitoring the relative concentration of particulates during the 14 tests in part III are given in Table XI.

There was no significant change in the particulate concentrations during the 2-hr test periods, under the stirred settling conditions in these experiments. As mentioned previously, about half the weight of the test dust was submicron carbon black, with a number median diameter of 0.025 μ. Three tests were made to collect material on glass and stainless steel slides, under conditions of both stirred and unstirred settling. The slides were situated in the lower part of the chamber, and were examined after being in the chamber for 24 hrs. Only about 10 particles greater

TABLE VII

CONCENTRATIONS OBTAINED IN TEST CHAMBER WHEN TESTING ATMOSPHERES CONTAINING THE MIXTURE OF GASES

GAS	AMOUNT INTRODUCED INTO CHAMBER, ppm by vol	EXPT'L DAY	SAMPLING TIME, min	CONCENTRATION, ppm by vol
Total aldehydes	0.60 (1.01 γ/liter)	9	0-25	0.09
		10	0-25	0.06
		10	30-55	0.08
		9	55-80	0.03
		10	60-85	0.05
		9	100-125	0.03
Acetic acid	0.40 (1.00 γ/liter)	7	0-15	none
		3	25-40	none
		7	30-45	none
		3	85-100	none
		7	100-115	none
		3	110-125	none
Acetylene	0.55 (0.60 γ/liter)	1	0-2	0.55
		1	35-37	0.93
		1	72-74	0.67
		1	97-99	0.76
		1	119-121	0.63
Ammonia	1.50 (1.08 γ/liter)	2	0-10	0.30
		2	15-25	0.22
		8	35-45	0.27
		8	45-55	0.25
		8	75-85	0.25
		2	100-110	0.19
Benzene + hexane	0.55 (1.65 γ/liter)	1	0-2	0.55
		1	35-37	0.33
		1	72-74	0.44
		1	97-99	0.49
		1	119-121	0.28
Carbon monoxide	10.0 (11.6 γ/liter)	4	0-5	10.0
		9	29-34	5.0
		4	58-63	5.0
		9	75-80	5.0
		4	110-115	5.0
		9	117-122	3.0

TABLE VII (*Continued*)

GAS	AMOUNT INTRODUCED INTO CHAMBER, ppm by vol	EXPT'L DAY	SAMPLING TIME, min	CONCENTRATION, ppm by vol
Hydrogen cyanide	0.15 (0.126 γ/liter)	3	0-20	0.15
		3	27-47	0.14
		7	42-62	0.11
		3	62-82	0.13
		7	86-106	0.14
		7	121-141	0.13
Hydrogen sulfide	0.20 (0.29 γ/liter)	4	0-30	0.24
		4	25-55	0.32
		6	35-65	0.24
		4	60-90	0.35
		6	75-105	0.29
		6	100-130	0.26
Nitrogen dioxide	1.00 (1.91 γ/liter)	11	0-10	0.9
		12	0-10	0.9
		11	30-40	0.35
		12	60-70	0.09
		11	100-110	0.09
		12	115-125	0.07
Ozone	2.00 (3.9 γ/liter)	2	0-5	2.16
		6	13-18	1.02
		2	30-35	0.48
		6	82-87	0.02
		2	102-107	0.008
		6	123-128	0.008
Sulfur dioxide	5.00 (13.2 γ/liter)	5	1-3	2.7
		5	6-8	1.1
		10	6-8	1.03
		10	12-14	0.15
		10	17-19	0.04
		5	32-34	0.03
Sulfuric acid	0.41 (1.65 γ/lit[illegible]	4	0-10	none
		7	20-30	none
		7	60-70	none
		4	70-80	none
		4	95-105	none
		7	110-120	none

TABLE VIII

SUMMARY OF RESULTS, PART II. MIXTURE OF GASES IN CHAMBER

GAS	EXPT'L DAY*	AMOUNT INTRODUCED, ppm	REGRESSION LINE $\log Y = b_0 + b_1 x$	DAY EFFECT	95% CONFIDENCE INTERVAL FOR TRUE SLOPE**
Total aldehyde	8	0.6	$\log Y = -1.0509 - 0.00491x$	none	+0.0057, -0.0155
	9	0.6	$\log Y = -1.1511 - 0.00131x$	none	+0.0122, -0.0148
	8 + 9		$\log Y = -1.0594 - 0.00472x$	--	+0.00026, -0.00826
Acetylene	1	0.55	$\log Y = -0.1688 + 0.00018x$	--	+0.00306, -0.00270
Ammonia	1	1.5	$\log Y = -0.56618 - 0.00156x$	none	+0.00291, -0.00603
	7	1.5	$\log Y = -0.55449 - 0.00064x$	none	+0.00221, -0.00353
	1 + 7		$\log Y = -0.54919 - 0.00126x$	--	+0.00049, -0.00301
Benzene + Hexane***	1	0.55	$\log Y = -0.30765 - 0.00126x$	--	+0.00223, -0.00479
Carbon monoxide	3	10.0	$\log Y = 0.96076 - 0.00278x$	none	+0.00368, -0.00924
	8	10.0	$\log Y = 0.81275 - 0.00248x$	none	+0.00407, -0.00903
	3 + 8		$\log Y = 0.91198 - 0.00298x$	none	-0.00566, -0.00030
Hydrogen cyanide	2	0.15	$\log Y = -0.81501 - 0.00099x$	none	-0.00122, -0.00075
	6	0.15	$\log Y = -0.99064 + 0.00097x$	none	+0.00495, -0.00301
	2 + 6		$\log Y = -0.85964 - 0.00026x$	--	+0.00106, -0.00158
Hydrogen sulfide	3	0.20	$\log Y = -0.63735 + 0.00262$	none	+0.00730, -0.00206
	5	0.20	$\log Y = -0.63828 + 0.00067$	none	+0.00517, -0.00383
	3 + 5		$\log Y = -0.57800 + 0.00040$	--	+0.00274, -0.00194
Nitrogen dioxide	14	1.0	$\log Y = -0.04596 - 0.00972x$	none	-0.01492, -0.00452
	15	1.0	$\log Y = -0.13125 - 0.00975x$	none	+0.00845, -0.02795
	14 + 15		$\log Y = -0.07968 - 0.00989x$	--	-0.01419, -0.00559
Ozone	1	2.0	$\log Y = 0.42038 - 0.02404x$	none	+0.01570, -0.06370
	5	2.0	$\log Y = 0.20306 - 0.01953x$	none	-0.03703, -0.00203
	1 + 5		$\log Y = 0.32419 - 0.02146x$	--	-0.02612, -0.01680
Sulfur dioxide	4	5.0	$\log Y = 0.51929 - 0.06209x$	present	-0.05169, -0.03649
	9	5.0	$\log Y = 0.89287 - 0.12862x$	present	-0.15882, -0.09842
	4 + 9		$\log Y = 0.35165 - 0.06711x$	--	-0.10731, -0.02691

* 3 samples of each of 2 gases collected on an experimental day, except hydrocarbons. 4 samples hydrocarbons collected.

** Regression was said to be present only if the confidence interval for the slope did not include zero.

*** Equal quantities of both hydrocarbons.

TABLE IX

CONCENTRATIONS OBTAINED IN TEST CHAMBER WHEN TESTING ATMOSPHERES CONTAINING THE MIXTURE OF GASES AND PARTICULATES

GAS	AMOUNT INTRODUCED INTO CHAMBER, ppm by vol	EXPT'L DAY	SAMPLING TIME, min	CONCENTRATION, ppm by vol
Total aldehydes	0.60 (1.0 γ/liter)	3	0-25	0.12
		5	10-35	0.14
		9	15-40	0.10
		9	55-80	0.09
		3	60-85	0.12
		3	90-115	0.10
		5	100-125	0.06
		9	100-125	0.08
		5	125-150	0.05
Acetic acid	0.40 (1.0 γ/liter)	7	0-15	none
		12	0-15	none
		12	30-45	none
		2	50-65	none
		7	60-75	none
		12	80-95	none
		2	100-115	none
		7	100-115	none
		2	115-130	none
Ammonia	1.50 (1.08 γ/liter)	2	0-10	0.32
		5	0-10	0.29
		10	20-30	0.22
		2	25-35	0.28
		5	45-55	0.28
		2	75-85	0.25
		10	75-85	0.20
		5	90-100	0.28
		10	120-130	0.25
Carbon monoxide	10.0 (11.6 γ/liter)	8	0-5	10.0
		6	5-10	7.5
		13	15-20	10.0
		6	30-35	10.0
		13	50-55	5.0
		8	60-65	7.5
		8	100-105	7.5
		6	115-120	10.0
		13	120-125	10.0
Hydrogen cyanide	0.15 (0.126 γ/liter)	10	0-20	0.12
		4	10-30	0.14
		8	15-35	0.10
		10	40-60	0.10
		4	60-80	0.09
		8	75-95	0.11
		10	90-110	0.09
		8	110-130	0.13
		4	120-140	0.10

TABLE IX (*Concluded*)

GAS	AMOUNT INTRODUCED INTO CHAMBER, ppm by vol	EXPT'L DAY	SAMPLING TIME, min	CONCENTRATION, ppm by vol
Hydrogen sulfide	0.20 (0.29 γ/liter)	1	0-30	0.24
		7	10-40	0.19
		3	30-60	0.31
		1	40-70	0.26
		7	70-100	0.30
		1	100-130	0.24
		7	110-140	0.29
		3	115-145	0.24
		3	145-175	0.24
Nitrogen dioxide	1.00 (1.91 γ/liter)	11	0-10	0.9
		13	0-10	0.8
		12	20-30	0.3
		13	30-40	0.25
		11	50-60	0.2
		12	55-65	0.1
		11	100-110	0.08
		13	110-120	0.09
		12	115-125	0.05
Ozone	2.00 (3.9 γ/liter)	4	0-5	1.80
		9	5-10	1.30
		1	30-35	0.90
		4	40-45	1.00
		9	45-50	0.50
		1	82-87	0.05
		9	90-95	0.005
		4	95-100	0.001 (trace)
		1	95-100	0.001 (trace)
Sulfur dioxide	5.00 (13.2 γ/liter)	6	0-3	3.3
		14	5-8	2.0
		6	11-14	2.2
		11	13-16	0.6
		11	18-21	0.1
		14	20-23	0.09
		6	20-23	0.12
		11	27-30	0.04
		14	30-33	0.05
Sulfuric acid	0.41 (1.65 γ/liter)	7	0-10	none
		12	0-10	none
		12	35-45	none
		2	50-60	none
		7	60-70	none
		12	80-90	none
		2	100-110	none
		7	100-110	none
		2	115-125	none

TABLE X

SUMMARY OF RESULTS, PART III. GASES AND PARTICULATES IN CHAMBER

GAS	EXPT'L DAY*	AMOUNT INTRODUCED, ppm	REGRESSION LINE, $\log Y = b_0 + b_1 x$	DAY EFFECT	95% CONFIDENCE INTERVAL FOR TRUE SLOPE**
Total aldehydes	3	0.6	$\log Y = -0.90045 - 0.00075x$	3 & 5	+0.00205, −0.00355
	5	0.6	$\log Y = -0.76951 - 0.0039\ x$	3 & 5	−0.00466, −0.00324
	9	0.6	$\log Y = -1.12566 - 0.00113x$	none	−0.00145, −0.00081
	3 + 5 + 9		$\log Y = -0.88200 - 0.00214x$	--	−0.00423, −0.00005
Ammonia	2	1.5	$\log Y = -0.49755 - 0.00136x$	none	+0.00009, −0.00281
	5	1.5	$\log Y = -0.53929 - 0.00016x$	none	+0.00024, −0.00056
	10	1.5	$\log Y = -0.69176 + 0.00050x$	none	+0.00401 −0.00301
	2 + 5 + 10		$\log Y = -0.54948 - 0.00061x$	--	+0.00057, −0.00179
Carbon monoxide	6	10.0	$\log Y = -0.91439 + 0.00084x$	none	+0.00477, −0.00309
	8	10.0	$\log Y = 0.98947 - 0.00131x$	none	+0.00116, −0.00376
	13	10.0	$\log Y = 0.86054 + 0.00061x$	none	+0.01441, −0.01319
	6 + 8 + 13		$\log Y = 0.92004 + 0.00008x$	--	+0.00268, −0.00252
Hydrogen cyanide	4	0.15	$\log Y = -0.87417 - 0.00125x$	none	+0.00435, −0.00685
	8	0.15	$\log Y = -1.03594 + 0.00114x$	8 & 10	+0.00269, −0.00041
	10	0.15	$\log Y = -0.91585 - 0.00136x$	8 & 10	−0.00265, −0.00007
	4 + 8 + 10		$\log Y = -0.93995 - 0.00041x$	--	+0.00088, −0.00170
Hydrogen sulfide	1	0.20	$\log Y = -0.60538 - 0.00004x$	none	+0.00145, −0.00153
	3	0.20	$\log Y = -0.66646 - 0.00104x$	none	+0.00012, −0.00220
	7	0.20	$\log Y = -0.74685 + 0.00195x$	none	+0.01035, −0.00645
	1 + 3 + 7		$\log Y = -0.61135 + 0.00019x$	--	+0.00126, −0.00088
Nitrogen dioxide	11	1.0	$\log Y = -0.03574 - 0.01051x$	none	+0.01584, −0.01685
	12	1.0	$\log Y = -0.60506 - 0.00784x$	none	+0.08950, −0.10530
	13	1.0	$\log Y = -0.14994 - 0.00893x$	none	+0.00150, −0.01930
	11 + 12 + 13		$\log Y = -0.16756 - 0.00951x$	--	−0.21586, −0.11926
Ozone	1	2.0	$\log Y = -1.34572 - 0.03936x$	none	+0.0361, −0.1149
	4	2.0	$\log Y = -0.75320 - 0.03549x$	none	+0.01250, −0.09350
	9	2.0	$\log Y = -0.62505 - 0.02945x$	none	+0.01080, −0.05960
	1 + 4 + 9		$\log Y = -0.79958 - 0.03342x$	--	−0.04523, −0.02162
Sulfur dioxide	6	5.0	$\log Y = -0.85132 - 0.07468x$	none	+0.07830, −0.22770
	11	5.0	$\log Y = -0.73842 - 0.07926x$	none	+0.04490, −0.20310
	14	5.0	$\log Y = -0.59623 - 0.06611x$	none	+0.00939, −0.14161
	6 + 11 + 14		$\log Y = -0.76066 - 0.07513x$	--	−0.09793, −0.05833

* 3 samples of each of 2 gases collected on an experimental day.

** Regression was said to be present only if the confidence interval for the slope did not include zero.

TABLE XI

RELATIVE CONCENTRATION OF PARTICULATE MATERIAL IN GAS-AEROSOL MIXTURES MONITORED IN PART III OF PROGRAM

TEST DAY	INITIAL READING*	READING AT 60 MIN	READING AT 120 MIN
1	1.00	1.00	1.00
2	1.00	1.01	1.02
3	1.00	0.99	1.00
4	1.00	1.02	1.02
5	1.00	0.97	0.98
6	1.00	0.98	0.98
7	1.00	0.97	0.98
8	1.00	1.03	1.06
9	1.00	1.02	1.04
10	1.00	0.98	0.97
11	1.00	1.01	1.03
12	1.00	1.01	0.99
13	1.00	1.00	0.99
14	1.00	0.98	1.02

* Maximum recorder deflection obtained within 3 secs after particulate injection in all cases. Readings normalized, with initial reading considered as unity after subtraction of background reading, obtained before injection. Initial readings were reproducible to ±1%.

than the limit of resolutions of the microscope were obtained on a slide. This was attributed to the very small amount of material (1.2 mg) initially injected. Two tests were made in which 100 mg of the mixture was injected, one under the stirred settling conditions, the other with the fan off. The slides were removed after 2 hrs, and were observed under the microscope. There were about 10 particles per sq mm, and the size distribution was essentially the same as that given in Table III. It is concluded, then, that under these experimental conditions, a stable suspension of particles in the submicron range was present during the 14 tests on part III.

D. Results of Combining Parts II and III

As shown in Tables VIII and X, the variability of the results proved to be too great in both parts II and III to permit distinguishing any effects of the aerosol on the gases in the mixture. The results obtained for each gas in the two parts were then combined to represent a total of 15 observations of each constituent, in order to obtain a better estimate of experimental error in monitoring the constituents, ignoring the infrequent day effects. The results are given in Table XII.

The minimum number of observations which would be required under these test conditions was then computed for each gas, accepting the slope variations given in Table XII as the range of experimental error which would be tolerated. The method of determining the minimum number of observations is given in Appendix D, "Statistical Treatment of Data." It was found that about 8 observations of a particular gas over a 2-hr period would be

TABLE XII

COMBINATION PART II (GASES ONLY) AND PART III (GASES + PARTICULATES)

15 Observations on Each Gas

GAS	AMOUNT INTRODUCED ppm	REGRESSION LINE LOG $Y = b_0 + b_1 x$	95% CONFIDENCE INTERVAL FOR TRUE SLOPE
Total aldehyde	0.6	$\log Y = -1.01262 - 0.00192x$	+0.00110, -0.00496
Ammonia	1.5	$\log Y = -0.55256 - 0.00080x$	+0.00007, -0.00167
Carbon monoxide	10.0	$\log Y = -0.91945 - 0.00130x$	+0.00075, -0.00335
Hydrogen cyanide	0.15	$\log Y = -0.90634 - 0.00037x$	+0.00064, -0.00138
Hydrogen sulfide	0.20	$\log Y = -0.58760 - 0.00012x$	+0.00026, -0.00050
Nitrogen dioxide	1.0	$\log Y = -0.13073 - 0.00969x$	-0.01167, -0.00771
Ozone	2.0	$\log Y = -0.52661 - 0.02695x$	-0.03390, -0.0200^
Sulfur dioxide	5.0	$\log Y = -0.53900 - 0.06867x$	-0.08747, -0.04987

required in order to obtain a slope of the accepted variability 95% of the time that the tests would be repeated under these conditions.

A single test for each constituent was made when the gas mixture with particulates was at 40% relative humidity. The sample were collected 15 minutes after injecting the test mixture. The results are given in Table XIII.

There were no gross effects of humidity obtained in these tests. Although minor effects of humidity on these gases would be expected to be present under the experimental conditions, they would not be expected to have practical significance. Determination of these effects would require a program similar to that of part III, but at the lower humidity.

TABLE XIII

TESTS OF GAS AND PARTICULATE MIXTURE
AT 40% HUMIDITY
(15 min after injection)

GAS	CONCENTRATION, ppm
Total aldehyde	0.10
Ammonia	0.35
Carbon monoxide	10.0
Hydrogen Cyanide	0.07
Hydrogen sulfide	0.27
Nitrogen dioxide	0.10
Ozone	1.20
Sulfur dioxide	1.00

V APPLICATION OF METHODS TO SCALED-UP CHAMBER SIZE AND TO COLLECTION OF SAMPLES IN BACTERIOLOGICAL SAFETY CABINETS

It is feasible to prepare the gas-aerosol mixtures in larger chambers and to monitor the constituents by the same methods used on part III of this program. However, due to different surface-to-volume relationships, different surface characteristics, differences in stirring conditions, and possible variations in the injection methods to suit future studies, the atmospheres in other test chambers should be monitored, using an experimental design similar to that used on part III of this program to determine the variation of concentration of materials in the chamber. A minimum of 9 observations of each gas should be obtained in order to assure the operator that the atmosphere is reproducible within the accepted variations described above.

It is feasible in all tests to operate under bacteriologically safe conditions. The bubblers could be situated in a bacteriological safety cabinet attached to the tank and subsequently could be transferred aseptically to a larger safety cabinet containing the analytical reagents and apparatus required for the particular analysis. The line from the sampler to the pump, the pump, and the waste line, could be gas-sterilized after an operation. Time would be required to attain proficiency in each analytical technique when using safety-cabinet gloves.

ACKNOWLEDGMENTS

Mr. Robert C. Goettelman, Physicist, constructed the injection apparatus and operated the injection system in parts I and II. He also assisted in the sampling and analytical program in parts I and II, and wrote Appendix C, which is concerned with the corrections in concentration for dilution in the chamber. Mr. Conrad Schadt tested sampling and analytical methods. Mrs. Donna Seppell, Chemist, carried out the sampling and analysis in parts II and III. Mr. Leonard Loving, Associate Mathematician, carried out the statistical analysis.

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Appendix A

GASEOUS TEST FORMULATION

Appendix A

GASEOUS TEST FORMULATION
(From Reference 1, Table D-I)

COMPONENT	SOURCE	MOLE WEIGHT	THEORETICAL CONCENTRATION[a]		THEORETICAL FEED: Total Component Per 2 x 10^3 liters[b]	
			Volume, ppm	Weight, ppm	Volume, cc	Weight, mg
Sulfur dioxide	Cylinder	64.06	1.0	2.2	20.0	
Sulfur trioxide	[c]	80.06	0.05			3.3 (H_2SO_4)
Hydrogen sulfide	Cylinder	34.08	0.2	0.24	4.0	
Nitrogen dioxide	Cylinder	46.01	0.9	1.43	18.0	
Ammonia	Cylinder	17.03	0.3	0.18	6.0	
Formaldehyde		30.03	0.3	0.31		7.5
Acetaldehyde		44.05	0.1	0.15		3.7
Acrolein		56.06	0.1	0.19		4.7
Acetylene	Cylinder	26.04	0.55	0.50	11.0	
Hexane-n		86.17	0.28	0.83		20.1
Benzene		78.11	0.27	0.71		17.0
Carbon monoxide	Cylinder	28.01	10.0	9.66	200.0	
Carbon dioxide	Cylinder	44.01	400.0	607.6	2000.0[d]	
Ozone	High voltage discharge	48.00	0.2	0.33	4.0	
Hydrogen fluoride	35% hydrofluoric acid	20.01	0.008	0.006	0.16	0.15
Acetic acid		60.05	0.2	0.42		9.98
Hydrogen cyanide	$Ca(CN)_2 + H_2SO_4$	27.03	0.1	0.07	2.0	

[a] At test chamber conditions which were assumed to be 20°C at 758.6 mm Hg (0°C). Dry air was assumed to have a molecular wt of 28.97.

[b] Chamber volume taken as equivalent to 2.406 x 10^3 g dry air per conditions of note (a).

[c] Included with particulate formulation since injection is accomplished by thermally induced bursting of glass ampule charged with 0.01 N H_2SO_4 solution.

[d] Volume added is in excess of the 300 ppm (vol) taken as typical atmospheric concentration.

APPENDIX B

METHODS OF SAMPLING AND ANALYSIS

Appendix B

METHODS OF SAMPLING AND ANALYSIS

1. Determination of Acetaldehyde and Acrolein*

I Discussion

Acetaldehyde and acrolein (acrylic aldehyde) in the test atmospheres were analyzed by a polarographic method developed at Stanford Research Institute for determination of carbonyl compounds in polluted atmospheres (a). In this method, the sample was absorbed in a scrubber containing semicarbazide solution. Acetaldehyde and acrolein concentrations were then determined polarographically in the form of reducible semicarbazones, the potential at which reduction occurred being characteristic of the compound.

II Collection of Sample

A. Sampling Device

The test air was sampled through a fritted bubbler containing 25 ml of semicarbazide solution. The bubbler contained a medium frit, and was 20 cm long and 3 cm in diameter.

B. Sampling Technique

The test air was sampled at a rate of 10 liters/min for 20 min.

III Analytical Method

A. Reagents and Apparatus

1. Semicarbazide solution. The semicarbazide solution was 0.1 molar in aqueous semicarbazide, sodium chloride, sodium acetate, and acetic acid. One liter of this solution was prepared.

2. Sargent Polarograph

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* Used only in Part I of program. The method was not useful for the mixture, due to interferences.

(a) Coulson, Dale M. Polarographic Determination of Semicarbazones. XV International Congress of Pure and Applied Chemistry (Analytical Chemistry), Lisbon, September 1956.

B. Procedure

Triton X-100, 0.0016%, was added to the sample as a maximum suppressor, 3-4 ml were transferred to the polarograph cell, and the polarogram was obtained.

All glassware was chemically cleaned, and finally rinsed with the electrolyte solution. A blank was run with each set of experiments to check for possible impurities in the chemicals in the semicarbazide solution.

C. Calculations

The polarographic sensitivity of the various low molecular weight aldehyde semicarbazones had been found to be essentially a constant (a), making possible a single sensitivity factor throughout the present work. This sensitivity factor is "I" in equation (I) which gives the relationship between wave height and semicarbazone concentration.

$$C_s = \frac{i_d}{I m^{2/3} t^{1/6}} \qquad \text{(I)}$$

In equation (I), C_s is the semicarbazone concentration (millimoles) in aqueous solution, i_d is the wave height or diffusion current in microamperes, I is the diffusion current constant (or polarographic sensitivity factor), m is the rate of mercury flow through the polarographic capillary in mg/sec, and t is the mercury drop time in seconds per drop. The value of I, the sensitivity factor, was found to be 7 ± 1 for a number of semicarbazones of low molecular weight aldehydes and ketones including acrolein and acetaldehyde (a).

The portion of the wave between -1.0 and -1.1 v vs SCE (saturated calomel electrode) is characteristic of semicarbazones of formaldehyde, acrolein, and crotonaldehyde. Acrolein reduces at -0.99 v vs SCE, and this diffusion current, i_d, was used to determine acrolein. Acetaldehyde contributes to the wave at a potential of -1.16 v vs SCE, and this diffusion current, i_d, was used to determine acetaldehyde.

The following equation was used to calculate the concentration of carbonyl compounds in ml:

$$V_c = C_s \times V \times 10^{-3} \times 82 \times T \qquad \text{(II)}$$

where V_c is the carbonyl gas volume in ml, C_s is the millimolar semicarbazone concentration in equation (I), V is the scrubber solution volume in ml, T is the test gas temperature, °K, and 82 is the value of the gas constant.

The concentration of carbonyl compounds in ppm by volume is given by the following equation:

$$C_{ppm} = \frac{V_c \times 10^6}{200 \times 10^3} \qquad \text{(III)}$$

If equations (I), (II), and (III) are combined, equation (IV) results; it states the relationship between the experimentally determined quantities and the carbonyl compound concentration in ppm.

$$C_{ppm} = \frac{82\ i_d\ v\ T}{200 \times 10^3\ I_m^{2/3} t^{1/6}} \qquad (IV)$$

D. Sensitivity

The estimated precision of this method is ± 20% of the value if about 90% or more of the aldehydes (or ketones) are C_6 or lower.

IV Suggestions When Sampling from 50,000-Liter Chamber

The method is directly applicable when determining aldehydes in chambers of 50,000 liters capacity, but it should be tested further for interferences.

2. Determination of Acetic Acid*

I Introduction

Acetic acid in the test chamber was measured by first absorbing the acetic acid in a solution containing glycerol and water, and then determining the acidity of the solution, using Fleisher methyl purple. The method has been described by Miller, Scherberger, Brockmyre, and Fassett (a). The original method is sensitive to 0.5 ppm acetic acid in air. It was modified on the present program to be sensitive to about 0.1 ppm acetic acid in air. Carbon dioxide in the air does not interfere with the analysis, but acid vapors do interfere.

II Collection of Sample

A. Sampling Device

The test air was sampled through a fritted bubbler containing 30 ml of absorbing solution containing Fleisher methyl purple indicator. The bubbler contained a medium frit, and was 20 cm long and 3 cm in diameter.

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* Used in Parts I, II, and III of program.

(a) Miller, Franklin, Richard Scherberger, Henry Brockmyre, and David W. Fassett. Determination of acetic acid in air. Am. Ind. Hyg. Assoc. Quarterly 17, (2) 221-224 (June, 1956).

D. Sampling Technique

The test air was sampled at a rate of 10 liters/min until the indicator turned pale blue, as described below. In these tests, the sampling period was about 15 minutes.

III Analytical Method

A. Reagents and Apparatus

1. Absorbing Solution. Distilled water, 495 ml, was mixed with 495 ml glycerol (Eastman Kodak Co. Catalogue No. 338). Ten ml Fleisher methyl purple* were added to the solution. Finally, 2 drops of Dow Corning Antifoam A was added.

2. Standard Acetic Acid Solution. Glacial acetic acid, 0.953 ml was diluted to 1 liter with distilled water. One ml of this solution contained 1 mg acetic acid.

3. Micropipette, 0.005-ml graduations.

B. Procedure

1. A chamber blank was obtained by drawing 150 liters of clean chamber air through 30 ml of the absorbing solution. This was the volume of air which would theoretically be required in these tests. The absorbing solution was then titrated with the standard acetic acid solution until a color change from green to purple was obtained; 0.28 ml of the standard acetic acid was required.

2. A reagent blank was obtained by titrating 30 ml of the absorbing solution as above; 0.28 ml of standard acetic acid solution were also required for this titration.

3. Test samples were then collected, allowing the air to bubble through the absorber solution just until a pale blue was obtained. The solution was then transferred to a 100-ml Ehrlenmeyer flask, and was carefully titrated to the first distinct purple, using the microburette.

C. Calculations

Each ml of standard contained 1 mg of acetic acid, and the mg of acetic acid in the sample was equal to the mg of acetic acid required to titrate 30 ml of the absorbing solution (in these tests, 0.28 mg), minus the mg of acetic acid required to titrate the sample from blue to purple. One mg/liter of acetic acid is equal to 408 ppm.

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* Fleisher Chemical Company, Benjamin Franklin Station, Washington 4, D.C.

D. Sensitivity

Under these conditions, the technique was sensitive to 0.05 ppm acid as acetic acid.

E. Suggestions when Sampling from 50,000-Liter Chamber

The method requires practice in order to obtain reproducible end-points. Due to interferences, the method is only useful to determine the "total acid" in the atmosphere when monitoring the complete gaseous mixture. The effect of sulfuric acid aerosol can be excluded by using a millipore filter.

3. Determination of Total Aldehyde as "Formaldehyde"*

I Discussion

Aldehydes react rapidly in an aqueous solution of sodium bisulfite to form nonvolatile sodium formaldehyde-bisulfite compounds, as in the following example of the reaction of formaldehyde:

$$HCHO + NaHSO_3 \longrightarrow H_2C\begin{matrix} \diagup OH \\ \diagdown OSO_2Na \end{matrix}$$

The derivative can be decomposed only when the solution is made distinctly alkaline. This property permits direct estimation of small amounts of aldehyde by destroying excess bisulfite with iodine at pH 6 to 7, liberating the sulfate combined as sulfoxylate by proper adjustment of the pH, and titrating the dissociated bisulfite with a standard iodine solution. In the method described below, the aldehyde complex is hydrolyzed instantaneously at room temperature by addition of sodium carbonate and sodium acetate, and the solution is then titrated to a stable, stoichiometric end point (a).

II Collection of Sample

A. Sampling Device

The test air was sampled through an impinger which was 12 cm long and 3 cm wide. The nozzle of the impinger was 0.3 cm from the base.

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* Used on Parts II and III of program.

(a) Goldman, F. H. and Herman Yagoda. Collection and Estimation of Traces of Formaldehyde in Air. Ind. Eng. Chem., 15, 377-378, June 15, 1943.

B. Sampling Technique

Test air was sampled through an impinger containing 10 ml of 1% sodium bisulfite at 4 liters/min for 25 min.

III Analytical Method

A. Reagents and Apparatus

1. Micropipette, 0.005-ml graduations

2. Sodium bisulfite, 1%

3. Starch solution, 1%

4. Iodine, 0.1 N

5. Iodine, 0.01 N. Standardize daily by titration against 0.05 N sodium thiosulfate.

6. Sodium thiosulfate, 0.05 N

7. Sodium carbonate buffer solution. Dissolve 80 g of sodium carbonate in about 500 ml water. Add 20 ml glacial acetic acid. Dilute to 1 liter.

B. Procedure

1. The sample was transferred to a 250-ml flask with 2 washings of 10 ml H_2O.

2. One ml of 1% starch solution was added.

3. The solution was titrated to a dark blue end-point with 0.1 N iodine.

4. Excess iodine was destroyed by adding 1 or 2 drops of 0.05 N sodium thiosulfate.

5. The solution was brought back to a faint blue end-point with 0.01 N iodine.

6. Twenty-five ml of sodium carbonate buffer solution was added.

7. Iodine, 0.01 N, was added to a faint blue end-point which persisted 10 secs.

C. Calculations

One ml of 0.01 N iodine solution is equivalent to 0.15 mg of aldehyde as "formaldehyde."

D. Sensitivity

Under these conditions, the technique was sensitive to about ±0.1 ppm total aldehyde as formaldehyde.

E. Suggestions when Sampling from 50,000-Liter Chamber

The polarographic method was more sensitive, and more specific for the aldehydes, when the aldehydes alone were present in the chamber. If possible, the polarographic method should be tested extensively for interferences in the presence of the total gaseous mixture. However, an operator who is skilled in polarography would be necessary for interpreting the interferences.

4. Determination of Ammonia*

I Discussion

Ammonia was determined by passing the test air through an impinger containing Nessler's reagent (a). Ammonia reacts with Nessler's reagent to produce a yellow-to-brown color resulting from the following reaction:

$$2(Hg\ I_2 \cdot 2\ KI) + NH_3 + 3\ KOH \longrightarrow Hg_2\ NHI \cdot OH + 7\ KI + 2\ H_2O$$

Formaldehyde interfered with the reaction under the experimental conditions used on this program. It was necessary to obtain the ammonia concentration by subtracting the determined concentration of formaldehyde from that of the ammonia when monitoring the gaseous mixture.

II Collection of Sample

A. Sampling Device

The test air was sampled through an impinger which was 12 cm long and 3 cm wide.

B. Sampling Technique

Twenty-five ml of 0.1 normal sulfuric acid were added to the impactor and 60 liters of test air were sampled at a rate of 6 liters per minute for ten minutes.

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* Used in Parts I, II, and III of program.

(a) F. H. Goldman and M. G. Jacobs. Chemical Methods in Industrial Hygiene. Interscience Publishers, Inc., N.Y. 1953, page 82.

III Analytical Method

A. Reagents and Apparatus

1. Nessler's Solution

Nessler's solution was obtained from a scientific supply house for this program.* It can be prepared in the laboratory according to the recipe given in ref. (a).

2. Model 402 E Lumetron colorimeter with 25-ml cell, 440-mμ filter.

B. Procedure

The test solution was transferred from the impactor to the 25-ml Lumetron cell, and 2.5 ml Nessler's solution were added. The solution was mixed, and then read in the colorimeter, using a 440 mμ filter. A previously prepared calibration curve was used to obtain the concentration of ammonia in ppm in the test sample. The calibration curve was obtained by adding known concentrations of ammonium sulfate to 0.1 N sulfuric acid, transferring 25-ml aliquots to the 25-ml cell, treating with Nessler's solution as described above, and obtaining a curve of concentration of ammonia vs. the log of transmittance. A stock solution of ammonium sulfate containing 7.09 γ ammonia per ml was diluted to obtain known concentrations of ammonia applicable to this program.

C. Sensitivity

Under the sampling and analyzing conditions described above, the method is sensitive to about 0.03 ppm (0.02 γ/liter ammonia).

IV Suggestions when Sampling from 50,000-Liter Chamber

The above technique should be satisfactory for determining the concentration of ammonia in chambers of 50,000-liter capacity.

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* Braun-Knecht-Heimann, Inc. 1400-16th St., San Francisco, California.

(a) F. H. Goldman and M. G. Jacobs. Chemical Methods in Industrial Hygiene. Interscience Publishers, Inc., N.Y. 1953, page 82.

5. Determination of Carbon Monoxide*

I Discussion

The only practical, noninstrumental method for detection of carbon monoxide which was available on this program was the modified Shepherd technique (a). The technique was developed by the National Bureau of Standards, and employs a granular, yellow indicating gel that turns green in the presence of carbon monoxide. The indicating gel is prepared from purified silica gel by the addition of palladium and molybdenum salts and the subsequent treatment described by Shepherd (b). A guard gel is used to remove interfering substances, particularly water vapor, from the gas to be tested, and test air is drawn through the indicator. The concentration of carbon monoxide is then determined directly by matching the color of the indicating gel with a color chart or set of standard indicating tubes.

Schuhknecht and Schinkel (c) have discussed the use of the NBS carbon monoxide indicator to estimate carbon monoxide in mine gases. The interference color changes produced by various test concentrations of hydrogen, paraffin hydrocarbons, and ethylene are described. The indicating gel is not sensitive to hydrogen or methane. The sensitivity to paraffin hydrocarbons increases with the number of carbon atoms in the hydrocarbon molecule, and reacts to give a dark zone at the point of initial gas contact with the indicating gel. The sensitivity to ethylene is very great; traces of ethylene produce a blue color in the indicating gel. The method was tested for interference by the initial concentration of hexane used on this program, 0.28 ppm. There was no interference under these test conditions. Interference by ethylene was not a problem because ethylene was not a component of the gaseous test mixture.

A modification of the method described above was tested on this program, but was not carried to completion because the above method proved satisfactory. This second method was developed by the Bureau of Mines, and consisted essentially of bringing a measured volume of air sample in contact with an acid solution containing palladium chloride, phosphomolybdic acid, and acetone. Molybdenum blue was produced by the reduction of the phosphomolybdic acid by carbon monoxide, and the concentration of carbon monoxide could be

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* Used in Parts I, II, and III of the program.

(a) Shepherd, Martin, Schuford Schumann, and Marthada V. Kilday. Determination of carbon monoxide in air pollution studies. Anal. Chem. 27, 380 (1955).

(b) Shepherd, Martin. Rapid determination of small amounts of carbon monoxide. Preliminary Report on the NBS colorimetric indicating gel. Anal. Chem. 13, 77 (1947).

(c) Schuhknecht, W. and H. Schinkel. Indicator ampoules for carbon monoxide and their use for the detection of carbon monoxide in mine gases. Glückauf, 87, 883-888, 1951. (In German).

determined colorimetrically (d). The method should be sensitive to ±1 ppm of carbon monoxide if 1000 ml of test gas are sampled.

II Collection of Sample

A. Sampling Device

A carbon monoxide detector made by the Mine Safety Appliances Company* was used. The device consists of a squeeze-bulb for drawing test air through one of the indicator tubes, and a color-matching scale to determine colorimetrically the concentration of carbon monoxide in the air sampled.

B. Sampling Technique

Indicator tubes for this instrument, containing a yellow silica gel, impregnated with a silica-molybdate compound and catalyzed by means of palladium sulfate, were also obtained from Mine Safety Appliances Co. (Cat. No. BY-47134).

III Analytical Method

The lower limit of reproducibility of the instrument is 10 ppm carbon monoxide when using the directions for sampling which accompany the instrument, i.e., when sampling 5 bulbfulls of test air. However, it was found that 10 bulbfulls of test air containing 5 ppm carbon monoxide produced the same indicator color as 5 bulbfulls of test air containing 10 ppm carbon monoxide, and that the range of sensitivity was ±2.5 ppm under these test conditions. This sensitivity was considered to be sufficiently high for this program.

IV Suggestions when Sampling from 50,000-Liter Chamber

Five-hundred-liter samples could be collected when monitoring the atmosphere in the 50,000-liter chamber. Under these conditions, the procedure described by Shepherd in ref. (a) could be followed if monitoring the carbon monoxide with an accuracy of ±.01 ppm was desired. If this method should not be directly applicable, the technique described in the Bureau of Mines Report (d), and outlined in Section I, above, may be used. It is simpler and more direct than Shepherd's method. However, if the initial concentration of carbon monoxide in the test air is 10 ppm, as it was on this program, the above method, using the Mine Safety Appliances instrument, should be satisfactory.

(d) Folis, R. D., L. B. Berger, and H. H. Schrenk. Colorimetric Determination of low concentrations of carbon monoxide by use of a palladium-chloride-phosphomolybdic acid-acetone reagent. Report of Investigations No. 3785. U.S. Bur. of Mines. November, 1944.

* Mine Safety Appliances Company. Braddock, Thomas & Meade Streets, Pittsburgh 8, Pa. Cat. No. BY-47133.

6. Determination of Formaldehyde*

I Discussion

Formaldehyde in the test chamber was determined by measuring the violet color which develops on heating with chromotropic acid in the presence of strong sulfuric acid (a). Formaldehyde and chromotropic acid react in an undetermined way to form a complex which is stable up to about 200°C. This characteristic permits separation from volatile interfering compounds that evaporate below 200°C. This characteristic also permits concentration of the sample by evaporation without loss of formaldehyde. Therefore, if the amount of formaldehyde in the original sample is too small for direct reading, a concentration step may be added. This step was not used on the present program, but is described below. It should be included if the concentration of formaldehyde falls below 0.1 γ per ml of sample.

II Collection of Sample

A. Sampling Device

A fritted bubbler was used to obtain formaldehyde samples. It was 20 cm long, 3 cm in diameter, and contained a medium frit.

B. Sampling Technique

Thirty-five ml of 0.1 N sodium hydroxide was transferred to the bubbler. Fifty-four liters of air were sampled through this solution at a rate of 3 liters/min for 5 min.

III Analytical Method

A. Reagents and Apparatus

1. Chromotropic acid, 1,8-dihydroxynaphthalene-3,6-disulfonic acid, Eastman Kodak (P-1613), 1.0% aqueous solution. Ten milliliters of the solution were prepared, filtered, and stored in a brown bottle. When this solution darkens it should be discarded and a fresh supply prepared. The disodium salt, Eastman Kodak (P-230) was used on this program.** The solution was prepared fresh daily.

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* Tested in Part I of the program. Interferences from acrolein and acetaldehyde present in Parts II and III.

(a) MacDonald, W. E., Jr. Formaldehyde in Air. A specific test. Amer. Ind. Hyg. Assoc. Q. 15 (3), 217-219, 1954.

** 4,5-dihydroxy-2,7-naphthalene disulfonic acid (disodium salt) Catalog No. P-230, Distillation Products Industries, Div. of Eastman Kodak Co., Rochester 3, N.Y.

2. Concentrated sulfuric acid.

3. Formaldehyde standard solution "A" containing 1.00 g formaldehyde per liter of 0.1 N sodium hydroxide. Solution keeps about two weeks.

4. Formaldehyde standard solution "B" containing 10.0 mg formaldehyde per liter. Dilute 10.0 ml of Formaldehyde Standard Solution "A" to one liter with distilled water. This solution contains 10.0 micrograms of formaldehyde per ml. It should be prepared shortly before use.

5. Lumetron, Model 402 E, with 25-ml cell and 550-mμ filter.

B. Procedure

A 10.0-ml aliquot of the sample was transferred from the bubbler to a 30-ml Ehrlenmeyer flask, 0.25 ml of 1.0% chromotropic acid reagent was added, and the solution was mixed. Fifteen ml concentrated sulfuric acid was added with caution, and thoroughly mixed. The sulfuric acid was added as soon as possible after the chromotropic acid had been mixed in the solution, as the chromotropic acid salt deteriorates rapidly. The solution was cooled to room temperature, at which time color development was complete. The solution was then transferred to the colorimeter cell, and the concentration of formaldehyde was read directly from a calibration chart. The calibration chart was prepared concurrently by treating a blank (35 ml 0.1 N sodium hydroxide), and 35-ml solutions containing 10 γ, 20 γ, and 30 γ formaldehyde respectively, in the same manner as the unknown. The calibration points were plotted as log transmittance vs. γ formaldehyde/35 ml solution.

C. Calculations

The reading from the calibration chart indicated the number of γ formaldehyde in 54 liters of test air, so 1/54 of this value equals the number of γ formaldehyde/liter; 1.227 γ formaldehyde is equivalent to 1 ppm formaldehyde by volume.

D. Sensitivity

Under the sampling conditions used in this program, the method is sensitive to 0.01 ppm formaldehyde, or to about ±3% of the initial concentration of 0.3 ppm in the test chamber. If the amount of formaldehyde is less than about 0.05 ppm, 0.25 ml of the chromotropic acid solution can be added to a suitable aliquot of the test solution, and the mixture concentrated by evaporation. It is then diluted to 10.0 ml with 0.1 N sodium hydroxide, followed by the procedure described above.

IV Suggestions when Sampling from 50,000-Liter Chamber

The method as described above is directly applicable to scaled-up test chambers.

7. Determination of Hydrocarbons: Hexane, Benzene, and Acetylene*

I Discussion

There were no directly suitable, noninstrumental techniques for the analysis of hexane, benzene, and acetylene in the concentration range (0.5 ppm and below) tested in this program. The MSA aromatic hydrocarbon detector** is sensitive to 5 ppm benzene under prescribed test conditions. The method was modified so that a much greater volume of air could be sampled, but the sensitivity could not be increased. The method of Moffett, Doherty, and Monkman (a) is based on the optical absorption, at selected ultraviolet wavelengths, of benzene in iso-octane. The method is simple and accurate, but is sensitive in the milligram rather than the microgram range of benzene. Other ultraviolet methods for benzene are more complex and would require freezeout samples on this program (b). Mass spectrometry (c, d) and gas-liquid partition chromatography (e) would require freezeout samples, expensive facilities, and highly-trained personnel. Hydrocarbons were determined semi-quantitatively in this program by infrared spectrometry (f). The method was rapid and simple, the results were reproducible, and no freezeout was required.

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* Used in Parts I and II of program at 40% relative humidity in chamber.

** Aromatic Hydrocarbon Detector Cat. No. DD-72075. Mine Safety Appliances Company, Braddock, Thomas, and Meade Sts., Pittsburgh 8, Pa.

(a) Moffett, P. A., T. F. Doherty, and J. L. Monkman. A Direct Method for the Collection and Determination of Micro Amounts of Benzene or Toluene in Air. Am. Ind. Hyg. Assoc. Q. 17, 186-188. June, 1956.

(b) Tunnicliff, D. D., R. R. Brattain, and L. R. Zumwalt. Benzene, toluene, ethylbenzene, O-xylene, m-xylene, and p-xylene determination by ultraviolet spectrophotometry. Anal. Chem. 21, 890-94, 1949.

(c) Walker, J. K., and C. L. O'Hara. Analysis of automobile exhaust gases by mass spectrometry. Anal. Chem. 27, 825-28, (1955).

(d) Brown, R. A. Compound types in gasoline by mass spectrometer analysis. Anal. Chem. 23, 430-7 (1951).

(e) Dimbat, Martin D., Porter, P. E. and Stross, F. H. Gas chromatography. Apparatus requirements for quantitative application of gas-liquid partition chromatography. Anal. Chem. 28, 290 (1956).

(f) Twiss, S. B., D. M. Teague, J. W. Bozek and M. V. Sink. Applications of infrared spectroscopy to exhaust gas analysis. J. Air Poll. Control Assoc. 5, 75 (1955).

II Collection of Sample

Test air was drawn from the chamber into the infrared spectrometer, as described below.

III Analytical Method

A. Procedure

Samples for determination of hydrocarbons were analyzed by infrared spectroscopy, using a Perkin-Elmer Model 12-C Spectrometer with a 10-meter absorption cell. The cell was first evacuated, and then filled with room air to furnish a background reference. The cell was evacuated again and filled with uncontaminated air from the chamber, i.e., air which did not contain test pollutants. This second background was obtained in order to compare the chamber air and the room air, and to furnish any necessary corrections for the subsequent test samples. After the hydrocarbons had been added, periodic samples were taken from the tank by first evacuating the absorption cell and then bleeding the required amount of sample into the cell through a polyethylene tube, until atmospheric pressure was reached. Six and one-half liters of air were required. The instrument was zeroed on room air prior to each tank sample to compensate for amplifier drift. In initial tests of the method, it was found that hexane and benzene could not be resolved separately. However, the concentration of hexane plus benzene could be obtained in the 18.25 - 17.80 region of the scan. These are arbitrary units which include the 3.42 micron C-H absorption band, on this instrument, which is the region in which C_6 hydrocarbons absorb. The infrared spectrometer has a low sensitivity for methane, ethylene, and acetylene at the 3.41-micron band. Concentrations of acetylene were obtained by observing the peak at the 13.7-micron absorption band, which was included in the 7.65-6.25 region of the scan on this instrument. The instrument settings used in these tests are given below.

COMPONENT	RESPONSE, (arbitrary units)	SPEED, (min per drum revolution)	SLIT WIDTH, (mm)	GAIN, (arbitrary units)	TEST SIGNAL, ROOM AIR (optical density units)	REGION OF SCAN (arbitrary units)
Hexane and Benzene	2	4	0.40	15-2	log 1/N = 0.21	18.25-17.80
Acetylene	4	4	2.0	20-8	log 1/N = 0.30	7.25- 6.75

Water vapor interferes with the test, and may damage the instrument if the humidity is higher than about 60%. It is therefore customary to fasten a tube of Drierite into the sample line entering the spectrometer cell to absorb moisture. Carbon absorption is minimized if the Drierite is heated to about 60°C (f). However, the concentration range tested on this program was so low that a Drierite column may have interfered significantly, and tests were made without the Drierite column by maintaining the chamber air at about 40% RH.

B. Calculations

By Beer's Law,

$$(1)\quad \frac{I}{I_o} = e^{-k\lambda^L}$$

where $k\lambda^L$ is the coefficient of absorption for a particular gas, dependent on wavelength (λ), path-length of cell (L), and concentration of test gas (C); where I_o is the background illumination, and I is the illumination through the sample. Or,

$$(2)\quad \ln \frac{I}{I_o} = -(k\lambda^L)\ (C),\ \text{or,}$$

$$(3)\quad \ln \frac{I_o}{I} = (k\lambda^L)\ (C)$$

If optical density (OD) is defined as $\log_{10} I_o/I$, then

$$(4)\quad \ln \frac{I_o}{I} = 2.303 \log_{10} \frac{I_o}{I},\ \text{or}$$

$$(5)\quad \log_{10} \frac{I_o}{I} = \frac{1}{2.303} \ln \frac{I_o}{I} = \frac{(k\lambda^L)\ (C)}{2.303} = (C)\ (\text{constant})$$

If $I_o = 1$ (normalized), then

$$(6)\quad OD = (C)\ (\text{const.}) = \log_{10} \frac{1}{I},\ \text{and}$$

$$(7)\quad \Delta OD = \left(\log_{10} \frac{1}{I}\right) \text{sample} - \left(\log_{10} \frac{1}{I}\right) \text{air, and}$$

$$(8)\quad \frac{C_t}{C_o} = \frac{\Delta OD(t)}{\Delta OD(o)} = \frac{(\log_{10} 1/I)\ \text{sample}\ (t) - (\log_{10} 1/I)\ \text{air}\ (t)}{(\log_{10} 1/I)\ \text{sample}\ (t=o) - (\log_{10} 1/I)\ \text{air}\ (t=o)}$$

where t = time in minutes.

C. Sensitivity

The method is only semi-quantitative when analyzing for hydrocarbons under the experimental conditions used on this program, and no calibration curve was obtained. The sensitivity to benzene plus hexane and acrolein in the 0.5-ppm range was estimated to be about ± 0.15 ppm, or $\pm 30\%$.

IV Suggestions when Sampling from 50,000-Liter Chamber

This method would be generally applicable to large chambers, but the sensitivity would be greatly increased by using the Perkin-Elmer Dual Long Path Cell for the Model 21 Spectrophotometer.*

8. Determination of Hydrogen Cyanide**

I Discussion

Hydrogen cyanide was determined on this program by absorbing it in dilute sodium hydroxide and then titrating with silver nitrate solution to the first indication of turbidity (a). The reaction is as follows:

$$2\ NaCN + AgNO_3 \longrightarrow NaAg(CN)_2 + NaNO_3$$

Potassium iodide was added to the absorbing solution before titration to increase the sharpness of the endpoint. The method was specific for hydrogen cyanide in the concentration range of materials tested on this program.

II Collection of Sample

A. Sampling Device

The test air was sampled through a fritted bubbler containing 15 ml of sodium hydroxide absorbing solution. It was 20 cm long, 3 cm in diameter, and contained a medium frit.

B. Sampling Technique

Test air was drawn through the bubbler at a rate of 10 liters/min for 20 min.

III Analytical Method

A. Reagents and Apparatus

1. Silver nitrate, 0.02 N. Dissolve 3.398 g silver nitrate in 1 liter distilled water.

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* The Perkin-Elmer Corporation, Norwalk, Connecticut.

** Used in Parts I, II, and III of program.

(a) Cupples, H. L. Determination of Hydrocyanic Acid in Air and in Air Carbon Dioxide Mixtures. Ind. Eng. Chem., Anal. Ed. 5, 50 (1933).

2. Absorbing Solution. Dissolve 5 g sodium hydroxide in [illegible] ml water.

3. Potassium iodide solution. Dissolve 2 g potassium iodide in 100 ml water.

4. Micropipette, to read 0.005 ml.

B. Procedure

The contents of the flask were washed into a 100-ml Shrlenmeyer flask with about 10 ml water, and 5 ml of potassium iodide solution were added. The solution was titrated with the 0.02 N silver nitrate until a permanent precipitate was produced. The endpoint was most easily reproduced by passing a condensed beam of light through the solution in a horizontal direction and titrating until a permanent Tyndall effect was observed.

C. Calculations

One ml of 0.02 N silver nitrate is equivalent to 1.08 mg hydrogen cyanide. One mg hydrogen cyanide per liter test air is 906 ppm by volume.

D. Sensitivity

Under these test conditions, the method was sensitive to about 0.02 ppm hydrogen cyanide.

IV Suggestions when Sampling from 50,000-Liter Chamber

The method is directly applicable to chambers of 50,000-liter capacity. However, the sensitivity would be increased by using an amperometric titration technique (a).

9. Determination of Hydrogen Fluoride*

I Discussion

Hydrogen fluoride in the atmosphere is frequently determined by passing the test air through an impactor containing water, and then determining the fluorine by direct titration with thorium nitrate, using sodium alizarin sulfanate as an indicator (b). The concentration of hydrogen fluoride in

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(a) Laitinen, H. A., W. F. Jennings, and T. D. Parks. Amperometric Titration of Cyanide with Silver Nitrate, Using the Rotating Platinum Electrode. Ind. and Eng. Chem., Anal. Ed. 18, 574-5 (1946).

* Used only in Part I of the program.

(b) Association of Official Agricultural Chemists. Official and Tentative Methods of Analysis, Ed. 7, Washington, D.C., The Association, [illegible], pp. 390-396.

the chamber air was 0.008 ppm (0.0072 γ/liter) in this program, and the entire chamber volume (2000 liters) would be required for a single analysis. A laboratory model of a continuous analyzer for hydrogen fluoride was used in order to determine the decay of hydrogen fluoride in the present program (a). The method is based on the selective quenching of the fluorescence of magnesium oximate by fluoride ion, and is sensitive to about ±0.0005 ppm fluoride in this concentration range. However, the instrument may be sensitive to such conditions as wide variations in temperature and humidity, as well as to a number of the materials in the test atmosphere used in the present program. For this reason, it is suggested that the direct titration method be used for monitoring hydrogen fluoride in chambers with a capacity of 50,000 liters or greater, although relatively long sampling periods will be required, and it will be impossible to obtain information on short-term variations in the fluoride concentration.

II Collection of Sample

A. Sampling Device

A bubbler was used to collect air samples. It was 35 cm long and 6-1/2 cm wide.

B. Sampling Technique

Two hundred ml of distilled water was placed in two bubblers. Samples were collected at a rate of 1 cfm for 1 hr. About 1700 liters of test air were drawn through each of the bubblers. The two 150-ml samples were then combined, and titrated as described below.

III Analytical Method

A. Reagents and Apparatus

1. 2 Burettes, 5-ml capacity. Subdivisions, 1/100 ml.

2. Flasks, titration, wide-mouth, 500-ml capacity.

3. Thorium nitrate, 0.1 N. Dissolve 13.805 g of hydrated thorium nitrate ($Th(NO_3)_4 \cdot 4\ H_2O$) in water and make up to 1 liter. Dilute to 1/10 this concentration for 0.01 N solution.

4. Sodium fluoride solution, 1 mg F per ml. Dry C.P. sodium fluoride at 105°C to a constant weight. Cool in a desiccator. Dissolve 2.210 g in distilled water and make up to 1 liter.

(a) Chaikin, S. W., C. E. Glassbrook, and T. D. Parks. Paper presented at 123rd meeting American Chemical Society, Los Angeles, California, March, 1953.

5. Sodium fluoride solution, 0.01 mg F per ml. Dilute 10 ml of solution (4) to 1 liter.

6. Sodium alizarin sulfanate, aqueous, 0.05%.

7. Sodium hydroxide solution, 0.05 Normal. Dissolve 2 g of sodium hydroxide in 1 liter of distilled water.

8. Hydrochloric acid, 0.05 Normal.

9. Buffer solution. Dissolve 2.0 g of sodium hydroxide in 40 ml of distilled water. Dissolve 9.50 g of monochloroacetic acid in 60 ml of distilled water. Slowly add the sodium hydroxide solution, with stirring, to the monochloroacetic acid solution. This solution is stable for five days.

B. Procedure

1. Standardization of Thorium Nitrate

Standardize the approximately 0.01 N thorium nitrate solution as follows. Pipette samples of standard sodium fluoride solution directly into titrating flasks, using concentrations of 2.5 to 250 γ fluorine. Make up to 400-ml volumes with distilled water from the same source as the water in the collecting impinger.

Add 1.00 ml of 0.05% alizarin red indicator and restore the pink color by adding 0.05 N sodium hydroxide solution drop by drop. Add 0.05 N hydrochloric acid dropwise until the pink color is just discharged.

Add 1.00 ml of monochloroacetic acid buffer solution and titrate with 0.01 N thorium nitrate solution to the appearance of a faint pink color.

Prepare a water blank by titrating 200 ml of the distilled water with 0.13 to 0.16 ml of thorium nitrate solution after the addition of the other reagents. Compare all the subsequent samples with this blank. Subtract the volume of thorium nitrate used on the blank from the volume used on each standard. Construct a table to relate the quantity of fluoride taken to the volume of thorium nitrate used.

Standards should be subjected to the same procedure as the samples and checked against similar concentrations titrated directly.

2. Treatment of Samples

Transfer the contents of the 2 impingers into the 300-ml titration flask. Add indicator, sodium hydroxide, hydrochloric acid, and buffer solutions in the same manner as described for the standardization of the thorium nitrate solution. Titrate the sample to the color produced in the titration blank. Titrate the blank and subtract the ml of thorium nitrate solution used by the blank from the ml used by the sample. Determine the micrograms of fluorine found in the sample by using the table which relates

the quantity of fluorine in the sample to the quantity of thorium nitrate used for the titration.

C. Calculations

Parts per million (by volume) of fluorine = micrograms fluorine/liter test air x 1.287.

D. Sensitivity

The above titration is sensitive to ±0.5 γ fluorine. Assuming no disappearance of hydrogen fluoride in the test chamber air, about 24 γ fluorine should be obtained in the combined sample under the test conditions of this program.

IV Suggestions when Sampling from 50,000-Liter Chamber

Water is essentially a perfect absorber for hydrogen fluoride, and it would be possible to sample at a higher rate when using the 50,000-liter chamber.

10. Determination of Hydrogen Sulfide*

I Discussion

Hydrogen sulfide reacts with cadmium salts to yield an insoluble yellow cadmium sulfide. The amount of sulfide is determined by titration with potassium iodate, followed by back-titration with sodium thiosulfate, using starch as an indicator (a).

This method is used frequently for the determination of low concentrations of sulfide ion in ammoniacal cadmium chloride absorber solutions. If sulfur oxides are present, the cadmium sulfide precipitate is separated by filtration to prevent interference. The filter paper (Whatman #40) is then transferred to the 10% hydrochloric acid solution mentioned below, and titrated. It was the experience of this laboratory that when titrating very low, i.e., microgram, quantities of cadmium sulfide such as were obtained in this program, the filter paper interfered with the titration. Much more reproducible results were obtained by omitting this step.

* Used in Parts I, II, and III of the program.

(a) Goldman, F. H. and M. B. Jacobs. Chemical Methods of Industrial Hygiene. Interscience Publishers, N.Y., 1953. Page 58.

II Collection of Sample

A. Sampling Device

An impinger was used to collect samples for the determination of hydrogen sulfide. It was found that cadmium sulfide would collect on a fritted plug or disc. The impinger was 12 cm long and 3 cm wide. The nozzle of the impinger was 0.3 cm from the base.

B. Sampling Technique

50 ml of 10% cadmium chloride ($CdCl_2 \cdot 2\text{-}1/2\ H_2O$) were transferred to the impactor. Test air was sampled at a rate of 4 liters per minute for 30 minutes.

III Analytical Method

A. Reagents and Apparatus

1. Hydrochloric acid, 10%

2. Cadmium chloride, 10% ($CdCl_2 \cdot 2\text{-}1/2\ H_2O$)

3. Potassium iodate solution, standard, 0.1 normal. Dissolve 0.7134 g of pure potassium iodate in distilled water and add 2 g of sodium hydroxide pellets. Add 10 g of potassium iodate free from iodide. After completing solution, adjust to room temperature and dilute to 2 liters in a volumetric flask.

4. Potassium iodate, standard, 0.005 normal. Prepare by accurate dilution of the 0.01 normal solution.

5. Sodium thiosulfate, 0.01 normal. Dissolve about 5 g of sodium thiosulfate pentahydrate in 2 liters of freshly boiled and cooled distilled water. Store in a clean Pyrex bottle. To standardize this solution, pipette 25 ml of the 0.01 normal standard iodate solution into a 300-ml Ehrlenmeyer flask. Add 200 ml of water and 20 ml of hydrochloric acid. Allow to stand one minute and then titrate with the thiosulfate solution. As the end-point is approached, add 10 ml of 0.2% starch solution and titrate carefully until the solution is colorless. The thiosulfate solution should be restandardized every two weeks.

6. Sodium thiosulfate, 0.005 normal. Prepare before use by accurate dilution of 0.01 normal standard thiosulfate.

7. Starch solution. Add a cooled aqueous suspension of 2 g of soluble starch to one liter of boiling water, cooled to room temperature, and store in a clean bottle.

8. Microburettes, 10 ml.

B. Procedure

1. Empty sample from impactor into 125-ml, glass-stoppered Ehrlenmeyer flask.

2. Add 25 ml 10% hydrochloric acid.

3. Add potassium iodate, 0.005 normal, immediately until an excess is obtained as indicated by yellow color. In tests in this program the yellow appeared in all cases after adding the first drop of potassium iodate and one ml of potassium iodate was added.

4. Stopper quickly and shake.

5. Add 10 ml starch solution.

6. Titrate with sodium thiosulfate, 0.005 normal.

C. Calculations

One ml sodium thiosulfate, 0.005 normal, is equivalent to 5 µeq. of hydrogen sulfide. One mg of hydrogen sulfide per liter of test gas is equivalent to 0.719 ppm by volume of hydrogen sulfide.

D. Sensitivity

Atmospheres containing an initial concentration of 0.29 micrograms hydrogen sulfide/liter (0.2 ppm) were tested in this program. Under the sampling conditions mentioned in II, above, the method was sensitive to ±0.025 ppm in an atmosphere containing 0.255 ppm, i.e., ±10%.

IV Suggestions when Sampling from 50,000-Liter Chamber

The apparent sensitivity in these tests depends on the amount of air sampled. It is suggested that the sampling device be scaled up by a factor of 2, and that about 8 liters of air per min be sampled for 30 min. This should double the sensitivity, i.e., it should be about ±5% under these test conditions.

11. Determination of Total Oxides of Nitrogen*

I Discussion

The phenoldisulfonic acid method of Beatty, Berger, and Schrenk (a) was used in preliminary tests to determine the total oxides of nitrogen on this project.

The phenoldisulfonic acid method of Beatty, Berger, and Schrenk was used in all parts of the program (a). It consisted essentially of absorption of the nitrogen oxides in an acid solution to form nitrous and nitric acids, followed by oxidation of the nitrous acid with hydrogen peroxide. The solution was then neutralized and evaporated to dryness. The residue, which contained the oxides of nitrogen as alkali nitrate, was brought into contact with a mixture of sulfuric and phenoldisulfonic acid, forming nitrophenoldisulfonic acid, which on reaction with ammonium hydroxide formed yellow tri-alkali nitrophenoldisulfonate. The intensity of the yellow color was proportional to the concentration of oxides of nitrogen in the air sample. The concentration of oxides of nitrogen was determined colorimetrically, using standards prepared in the same manner.

The automatic instrument used for most of the tests in this program employs a diazotization process for determining nitric oxide and nitrogen dioxide continuously. Two special absorbers are used for the absorption of nitrogen dioxide in a solution of 0.5% sulfanilic acid and 20 ppm of N-(1-naphthyl) ethylenediamine dihydrochloride in 14% acetic acid, followed by colorimetric reading. One absorber measures the nitrogen dioxide alone; the other measures nitrogen dioxide plus nitric oxide after the nitric oxide has been oxidized by potassium permanganate. Standard error of the instrument is ±5% in the range of atmospheric concentrations of nitrogen oxides.

The method using phenoldisulfonic acid is described below. This method was used because the sampling and analytical technique had been developed for a previous project. However, the colorimetric method of Saltzman (b) was also used to test individual samples. It was a more rapid method, and more sensitive than the phenoldisulfonic acid techniques under the conditions of this program.

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* Tested in Part I, but not used because it is more complex than the Saltzman method which follows.

(a) Beatty, R. L., L. B. Berger, and H. H. Schrenk. Determination of the Oxides of Nitrogen by the phenoldisulfonic acid method. U.S. Bur. Mines Report of Investigations R.I. 3687. February, 1943.

(b) Saltzman, B. E. Colorimetric determination of nitrogen dioxide in the atmosphere. Anal. Chem. 26, 1949-55 (1954).

II Collection of Sample

A. Sampling Device

The test air was sampled through a fritted bubbler containing 50 ml of 0.1 N sodium hydroxide. The bubbler contained a medium frit, and was 20 cm long and 3 cm in diameter.

B. Sampling Technique

Fifty liters of air were drawn through the absorber solution at a rate of 10 liters per min.

III Analytical Method

A. Reagents and Apparatus

1. Phenoldisulfonic Acid Solution. This reagent was obtained from a local chemical supply house.* It is prepared as follows: Dissolve 25 g of pure white phenol in 150 ml of concentrated sulfuric acid. Add 75 cc of fuming sulfuric acid and heat at 100°C for two hours.

2. Hydrogen Peroxide, 3% Solution. Obtain a 30% hydrogen peroxide reagent which is low in nitrogen and dilute 10 ml to 100 ml with distilled water. Prepare fresh daily.

3. Potassium hydroxide, 1 normal.

4. Sulfuric acid, 1 normal.

5. Ammonium hydroxide, concentrated.

6. Standard potassium nitrate solution, stock. Dry potassium nitrate in an oven at 105 ±5°C for two hours. Dissolve 0.440 ±0.001 grams of salt in water and dilute to 1 liter. One ml of this solution is equivalent to 0.200 mg of nitrogen dioxide.

7. Standard potassium nitrate solution, dilute. Dilute 50 ml of stock potassium nitrate solution, above, to 250 ml with water and mix well. One ml of this solution is equivalent to 0.040 mg of nitrogen dioxide.

8. Model 402 E. Lumetron with 25-ml cell and 410-mμ filter.

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* Braun-Knecht-Heimann Company, 1400-16th Street, San Francisco, California.

9. pH test paper. This paper or series of papers should be capable of indicating the pH in the range of fairly high acidity and in the neutral range, such as pHydrion papers A or B.

B. Procedure

1. The 0.1 N sodium hydroxide was transferred to a 250-ml beaker. The bubbler was rinsed twice with 25 ml of water, and the washings were transferred to the beaker.

2. One ml of 3% hydrogen peroxide was added to the beaker, and the solution was acidified to a pH of about 1, using 1 N sulfuric in 1-ml portions.

3. The solution was heated to boiling, and 1 N sodium hydroxide was added to a pH of 8 or higher.

4. The solution was carefully evaporated to dryness, and 1 ml of phenoldisulfonic acid was added with rapid stirring while the test material was still hot.

5. About 5 ml water was added, and the salts were dissolved by mixing.

6. Concentrated ammonium hydroxide was added to excess as indicated by yellow color and odor of ammonium hydroxide.

7. The solution was filtered into the Lumetron cell, and the transmittance was determined, using a 410-mμ filter. The concentration of nitrogen oxides as NO_2 was read directly from a calibration curve prepared previously from the dilute standard potassium nitrate solution. Known amounts of the potassium nitrate were added to 50-ml portions of 0.1 normal sodium hydroxide, and were subjected to the procedure described above. The calibration curve covered the range 100 γ to 10 γ nitrogen dioxide.

8. A blank, consisting of 50 ml of 0.1 N sodium hydroxide, was run through all the steps with each set of standards and unknowns.

C. Calculations

One γ nitrogen dioxide is equivalent to 0.53 ppm by volume.

D. Sensitivity

The initial concentration of nitrogen dioxide in the chamber was 0.9 ppm by volume (1.72 γ/liter). The maximum concentration of nitrogen dioxide in each sample collected was 1.72 x 50, or 86 γ. The analytical method has a sensitivity under these test conditions of ±10% over the range 100 γ to 10 γ nitrogen dioxide.

IV Suggestions when Sampling from 50,000-Liter Chamber

The method is directly applicable to larger chambers. However, a higher sensitivity could be obtained if the size of the bubbler were doubled, and 100 ml of absorber were used. In this case, the flowrate through the bubbler could be increased to 20 liters/minute, and 10-min samples could be obtained as above. In addition, it would be possible to use this larger system and shorten the sampling period to 5 min. In this case, the sampling period would be cut in half, but the sensitivity would remain unchanged.

12. Determination of Nitrogen Dioxide*

I Discussion

Nitrogen dioxide was determined by the colorimetric method of Saltzman (a). In this method the sample is collected in a fritted bubbler by absorption in sulfanilic acid solution containing a coupling agent, and acetic acid as a foaming agent. This produces color directly and is specific for nitrogen dioxide in the concentration range of materials tested in this program. The method has a sensitivity in the parts per hundred million range.

II Collection of Sample

A. Sampling Device

The bubbler used in these tests contained a medium frit, and was 20 cm long and 3 cm in diameter.

B. Sampling Technique

Twenty-five ml of the Saltzman reagent were transferred to the bubbler and sampled at a rate of 0.6 liters/min for 10 min.

III Analytical Method

A. Reagents and Apparatus

1. Absorbing solution: 5 g of sulfanilic acid were dissolved in almost a liter of boiling water containing 140 ml of glacial acetic acid and 20 mg of N-(1-naphthyl)-ethylenediamine dihydrochloride.

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* Used in Parts I, II, and III of program.

(a) Saltzman, B. E. Colorimetric Microdetermination of Nitrogen Dioxide in the Atmosphere. Anal. Chem. 26, (12), 1949-1955 (1954).

2. Lumetron, Model 402 E, with 580-mμ filter and 25-ml cell.

B. Procedure

The test solution was transferred to a 100-ml flask and stoppered. Fifteen minutes were allowed for full color development and the solution was then transferred to the Lumetron cell. The concentration was determined from a previously prepared calibration curve. A blank of the absorbing solution was used throughout.

The calibration curve was obtained by adding known concentrations of sodium nitrite to the absorbing solution and plotting the log of the transmittance vs. the concentration of the sodium nitrite. The nitrogen dioxide dismutation ratio is 0.72; therefore, 2.03 μg/ml of sodium nitrite was equivalent to 1 ppm nitrogen dioxide (1.88 μg/liter of nitrogen dioxide).

13. Determination of Ozone*

I Discussion

Ozone was determined by passing the test air through a bubbler containing a buffered solution of potassium iodide, and then measuring the amount of iodine liberated (a, b). The reaction proceeds as follows:

$$O_3 + 2\ KI + H_2O \longrightarrow O_2 + 2\ KOH + I_2 \qquad (I)$$

The authors referenced above found that reactions of nitrogen oxides, peroxides, and chlorine which produce iodine proceed only to a very limited extent at low concentrations and at pH 7.0, because of the lack of hydrogen ions. The method described below is frequently used for the determination of atmospheric ozone. The absorption efficiency of ozone in the potassium iodide solution is very high under these test conditions, but if air is sampled too rapidly, released iodine may distill out of the solution, and low values for ozone may be obtained.

II Collection of Sample

A. Sampling Device

An impinger was used to collect the samples. The impinger was 12 cm long and 3 cm wide, with the nozzle 0.3 cm from the base.

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* Used in Parts I, II, and III of program.

(a) Crabtree, James, and A. R. Kemp. Accelerated ozone weather test for rubber. Ind. & Eng. Chem., Anal. Ed. 18, 769-74 (1946).

(b) Gluckauf, E., H. G. Neal, G. R. Marten, and F. A. Paneth. Measurement of the Local Concentration of Atmospheric Ozone. J. Chem. Soc., 1944, 1.

B. Sampling Technique

Twenty-five milliliters of the buffered solution of potassium iodide (described below) were added to the bubbler. Air from the chamber was sampled through the bubbler at a rate of 8 liters/min for 5 min.

III Analytical Method

A. Reagents and Apparatus

1. Buffered Potassium Iodide. Add 500 ml. of 0.025 N disodium hydrogen phosphate to 500 ml. 0.025 N potassium dihydrogen phosphate. Dissolve 20 g of potassium iodide in this solution.

2. Model 402 E Lumetron Colorimeter with 25-ml cell, 420-mμ filter.

B. Procedure

The test solution from the impactor was transferred to the Colorimeter cell, and the concentration of ozone was read from a previously prepared calibration curve of ppm ozone *vs.* log transmission. A No. 420 filter was used. The calibration curve was prepared as follows.

The initial concentration of ozone in the test chamber was 0.2 ppm, or 0.39 γ/liter. Forty liters of test air, containing a maximum of 15.6 γ ozone, were passed through the test bubbler. From the equation given in I, above, this amount of ozone would liberate 83.1 γ iodine. A stock solution was made up which consisted of 3.32 mg iodine per liter of buffered potassium iodide prepared as above. Twenty-five milliliters of this solution contain 83.1 micrograms of I_2, and the transmittance reading of this solution represented 0.2 ppm ozone in the test chamber. The solution was diluted to obtain other points for the calibration curve.

C. Sensitivity

Under the sampling and analytical conditions described above, the method is sensitive to about ±0.02 ppm (1.6 γ/liter) ozone.

IV Suggestions when Sampling from 50,000-Liter Chamber

The method is directly applicable to chambers of greater volume.

14. Determination of Sulfur Dioxide*

I Discussion

Sulfur dioxide was determined by the method of Paulus, Floyd, and Byers (a). In this test, sulfur dioxide is absorbed in an impinger containing a solution of sodium hydroxide and glycerine. This solution is used to inhibit oxidation to sulfate. A basic fuchsin-formaldehyde color reagent is then added, and the amount of sulfur dioxide is determined colorimetrically. The reproducibility of the method in the concentration range required on this project is ±2%.

II Collection of Sample

A. Sampling Device

The air was sampled through an impinger which was 12 cm long and 3 cm wide.

B. Sampling Technique.

Twenty-five ml of the absorbing solution were transferred to the impinger. Air from the chamber was sampled at a rate of 5 liters/min for 2 minutes.

III Analytical Method

A. Reagents and Apparatus

1. Absorbing solution: sodium hydroxide, 0.05 N, containing 2% glycerol.

2. Color reagent, stock solution No. 1: Shake a mixture of 480 ml water, 44 ml concentrated sulfuric acid, and 16 ml of a 3% solution of basic fuchsin in ethyl alcohol. Add 280 ml water and 4 g of Norite A activated carbon. Shake and refrigerate overnight. Filter to remove carbon. If this solution is refrigerated, it will remain stable for several months.

3. Color reagent, stock solution No. 2: Dilute 5 ml of 40% formaldehyde to 100 ml with water.

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* Used in Parts I, II, and III of program.

(a) Paulus, H. J., E. P. Floyd, and D. H. Byers. Determination of sulfur dioxide in atmosphere samples. Ind. Hyg. Assoc. Q. 15(4), 277-280(1954).

4. Working color reagent: Add 1 part of stock solution No. 2 to 10 parts stock solution No. 1. Mix, shake, and allow to stand 30 min before using.

5. Lumetron, Model 402 E, with 580-mμ filter and 25-ml cell.

B. Procedure

The test solution was transferred from the impinger to a 100-ml flask and stoppered. Working color reagent, 2.5 ml, was added, and the solution was allowed to stand 15 minutes for full color development. The solution was then transferred to the 25-ml Lumetron cell, and the concentration of sulfur dioxide was determined from a previously prepared calibration curve. A blank consisting of 25 ml of the absorbent solution was treated the same as the sample, and was carried through the analytical procedure.

The calibration curve was obtained by preparing known dilutions of sulfur dioxide in nitrogen in a continuous-stream gas-handling system, and allowing the stream of diluted sulfur dioxide to flow through 25 ml of the absorbing solution in the impactor for a fixed period of time. The solution was then treated with working color reagent as described above, and the transmittance was determined in the Lumetron. A curve was then prepared of the transmittance against the micrograms of sulfur dioxide in the sample. The points on the calibration curve were as follows:

Micrograms SO_2 in Sample	Lumetron Transmission Reading, %
none	100
10.8	87
16.2	61
27.0	40
37.8	32
54.0	20
81.0	12

C. Calculations

2.60 γ sulfur dioxide per liter of test gas is equivalent to 1.0 ppm sulfur dioxide.

D. Sensitivity

The initial concentration of sulfur dioxide in the test chamber was 1.0 ppm, or 2.64 γ/liter. The total flow of test air through the impactor was 10 liters, giving a maximum of 26.4 γ in the absorber solution. The sensitivity of this method over the range 26.4 γ to 2.64 γ is ±10%.

IV Suggestions when Sampling from 50,000-Liter Chamber

The method as described above is directly applicable to tests in chambers of 50,000-liter capacity.

15. Determination of Sulfuric Acid*

I Discussion

Sulfuric acid has an extremely low vapor pressure at room temperature, and exists as droplets in polluted atmospheres. A titrimetric method developed at Stanford Research Institute was used for the determination of sulfuric acid aerosol in the test chamber. The droplets collected quantitatively on Millipore filters.** The filter was then washed into a flask, and the sulfuric acid was determined by titration.

II Collection of Sample

A. Sampling Device

A Millipore filter, Type AA, white, plain, was connected in the chamber onto the sampling probe used in the other tests.

B. Sampling Technique

The test atmosphere was drawn through the filter at a rate of 10 liters per min for 10 min.

III Analytical Method

A. Reagents and Apparatus

1. Sodium hydroxide, approx. 0.01 N. Dissolve 0.5 g sodium hydroxide in 1 liter boiled distilled water.

2. Sodium hydroxide standard, 0.001 N. Dilute 10 ml sodium hydroxide, 0.01 N, to 1000 ml in a volumetric flask, using freshly boiled, distilled water. Titrate with standard sulfuric acid.

3. Methyl purple indicator solution.***

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* Used in Parts I, II, and III of program.

** Millipore Filter Corporation, Watertown 72, Mass.

*** Methyl-purple Indicator, Fleisher Chemical Co., Benjamin Franklin Station, Washington 4, D.C.

4. Millipore filter holder and type AA, white, plain, Millipore filters.

5. Microburette.

B. Procedure

The sulfuric acid on the filter was washed into a 100-ml Ehrlenmeyer flask with two 10-ml portions of boiled, distilled water. The solution was titrated with 0.001 N sodium hydroxide, using a microburette and methyl purple indicator. One drop of the indicator was used.

C. Calculations

One ml of the 0.0001 N sodium hydroxide contains 4 γ of sodium hydroxide, and will neutralize 4.9 γ sulfuric acid. Methyl purple is basic, and one drop will neutralize 7 γ of sulfuric acid. This amount was added to the calculated concentration of sulfuric acid.

D. Sensitivity

The method is sensitive to about 10 γ sulfuric acid under these test conditions.

IV Suggestions when Sampling from 50,000-Liter Chamber

The method should be directly applicable to test chambers of greater volume.

Appendix C

METHOD OF CORRECTION OF GAS AND PARTICULATE CONCENTRATION FOR DILUTION IN CHAMBER DUE TO SAMPLING

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METHOD OF CORRECTION OF GAS AND PARTICULATE CONCENTRATION FOR DILUTION IN CHAMBER DUE TO SAMPLING

The derivations of the equations used to correct the results obtained by chemical analysis for dilution in the chamber due to sampling are given below, followed by an example of the corrections in each phase of the program.

I Derivation of Equations

A. Changes in Concentration of a Test Gas Contained in a Volume V

1. Concentration changes due to sampling, assuming replacement by clean air, and instant mixing.

$$\text{Change in concentration} = -\frac{\text{change in test gas mass}}{\text{total gas vol.}}$$

$$dC = \frac{dM}{V} = -\frac{CQdt}{V}$$

$$\int_{C_o}^{C_t} \frac{dC}{C} = -\int_{t_o}^{t} \frac{Qdt}{V}$$

so

$$\ln \frac{C_t}{C_o} = \frac{-Qt}{V}$$

where

$$t_o = 0$$

or

$$C_t = C_o\, e^{\frac{-Qt}{V}} \qquad (1)$$

where

C_t = Conc. of test gas at any time (t)

C_o = initial conc. of test gas

Q = sampling rate

t = sampling time

V = total volume of contained test gas

M = mass

2. Concentration changes due to natural test gas decay only within the chamber.

Let k = coeff. of decay of any particular gas; then:

$$dC = -Ckdt$$

$$\int_{C_o}^{C_t} \frac{dC}{C} = -\int_{t_o}^{t} kdt$$

or

$$\ln \frac{C_t}{C_o} = -kt$$

where

$$t_o = 0$$

so

$$C_t = C_o e^{-kt} \qquad (2)$$

B. Dilution of a Contained Gas by Sampling and Natural Decay

Define dilution (D) as:

D = initial concentration - conc. at a time (t)

$D = C_o(t = 0) - C_t$

1. Dilution due to sampling, (D_s); as defined for k = 0

$$D_s = C_o - C_t = C_o - C_o e^{\frac{-Qt}{V}} = C_o\left(1 - e^{\frac{-Qt}{V}}\right) \qquad (3)$$

from Eq. (1)

2. Dilution due to natural decay, (D_d); as defined for $D_s = 0$

$$D_d = C_o - C_t + C_o - C_o e^{-kt} = C_o(1 - e^{-kt}) \qquad (4)$$

from Eq. (2)

C. Concentration of a Contained Gas at Time (t) with Both Natural Decay and Sampling Decay Operating Simultaneously

Let $C_t = C_o$ at $t = 0$ then as before,

$$\ln C_t = \ln C_o - kt - \frac{Qt}{V}$$

$$\ln C_t = \ln C_o - t\left(k + \frac{Q}{V}\right)$$

$$C_t = C_o\, e^{-t\left(k + \frac{Q}{V}\right)}$$

which may be written:

$$C_t = C_o\left[1 - \left(1 - e^{-kt} \cdot e^{\frac{-Qt}{V}}\right)\right]$$

or also

$$C_t = C_o\left[1 - \left(1 - e^{-kt}\right) - \left(1 - e^{\frac{-Qt}{V}}\right) + \left(1 - e^{-kt}\right)\left(1 - e^{\frac{-Qt}{V}}\right)\right]$$

From Eqs. (3) and (4) we see this is:

$$C_t = C_o - D_d - D_s + \frac{D_d D_s}{C_o} \qquad (5)$$

When sampling and natural decay occur simultaneously, D_s and D_d are good approximations of the dilutions due to sampling and decay if $D_d D_s / C_o$ is small compared with D_d and D_s.

Equation (5) can be written:

$$D_d = \frac{C_t + D_s - C_o}{\left(\frac{D_s}{C_o} - 1\right)} \qquad (6)$$

and from our previous definitions we can see that:

$$D_d = -\frac{C_t - C_o\, e^{-Qt/V}}{e^{-Qt/V}}$$

$$e^{-kt} = 1 + \frac{C_t - C_o\, e^{-Qt/V}}{C_o\, e^{-Qt/V}}$$

$$-k = \frac{\ln\left[1 + \frac{C_t - C_o\, e^{-Qt/V}}{C_o\, e^{-Qt/V}}\right]}{t}$$

which is:

$$k = -\left[\frac{1}{t} \ln \frac{C_t}{C_o} + \frac{Q}{V}\right] \tag{7}$$

In general, dilution due to sampling will be intermittent rather than continuous over long time intervals.

During times of no sampling: $D_s = 0$

$$\frac{D_d D_s}{C_o} = 0$$

Eq. (5) becomes $C_t = C_o - D_d$ and since when $D_s = 0$ $Q = 0$ we see Eq. (7) becomes:

$$k = \frac{\ln \frac{C_t}{C_o'}}{t} \tag{8}$$

where

$C_o' = C_t$ as defined in Eq. (5)

t = time of no sampling

The preceding development is, of course, true only when there is a single gas present in the test chamber.

Poly-gas Systems

If many gases are present in the same chamber we may expect reactions as follows:

$$(\nu_A)A + (\nu_B)B + (\nu_C)C + \ldots \rightleftarrows (\nu_L)L + (\nu_M)M + (\nu_N)N + \ldots$$

where ν_A, ν_B, etc., represent the number of molecules of reactant A, B, etc. and ν_L, ν_M, etc., the number of molecules of products L, M, etc.

Thus, for a particular gas A in such a mixture during periods of sampling we could write, for the initial reaction,

$$dC^A = \left[-C^A \frac{Q}{V} - C^A k^A + f\ (C^A, C^B \ldots)\right] dt \tag{9}$$

where C^A = Conc. of gas A, C^B = conc. of gas B, etc.

As might be expected, $f\ (C^A, C^B, \ldots)$ is an exceedingly complicated function which makes an exact solution of Eq. (9) quite unlikely.

As reaction products increased in concentration, Eq. (9) would have to be replaced by an even more complicated expression.

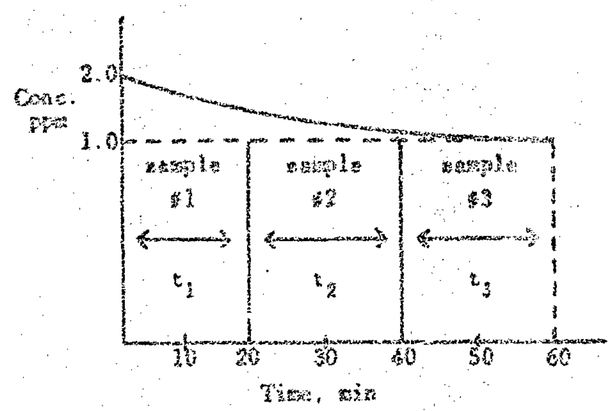
II Example of Corrections Used in Phase I of the Project

Two ppm of gas A were injected into a 2000-liter chamber at t_0. Chemical analysis of the gas was obtained by sampling the chamber air through a scrubber for 20 min at 10 liters/min. An equal volume of fresh air was drawn into the chamber during the sampling period.

As an example, the analysis indicated that there was 1.0 ppm of gas A in the chamber at t_{40-60}.

1. Correct the measured gas concentration for the approximate amount lost due to sampling over the 60-min interval.
2. Determine the approximate value of coefficient of gas decay (k).
3. Predict what conc. of gas A might be expected in the chamber at the end of a 2-hour period
   a. Assuming continuous gas sampling
   b. Assuming no gas sampling.

1. Solution



By Eq. (3) $D_s = C_0\ (1 - e^{-Qt/V})$

D_s = dilution due to sampling

C_0 = 2 ppm

Q = 10 liters/min

V = 2000 liters

$t = t_1 + t_2 + \frac{1}{2}\, t_3 = 50$ min

Note: the value $t_3/2$ is correct since the measured value of 1 ppm is the average between $C_{40\ min}$ and $C_{50\ min}$.

Thus,

$$D_s \approx (2)(1 - e^{-0.25}) = (2)(0.221) = 0.442 \text{ ppm}$$

$$\text{Conc.}_{corr.} = \text{conc.}_{meas.} + D_s$$

$$\text{conc.}_{meas.} = 1.0 \text{ ppm at } t = 50 \text{ min}$$

$$\text{conc.}_{corr.} = 1.0 + 0.442 = 1.442$$

2. Solution

By Eq. (7) $k \approx -\left[\frac{1}{t}\ \ln \frac{C_t}{C_0} + \frac{Q}{V}\right]$

where $C_t = C_{50} = C$ measured $= 1$ ppm so

$$k = -\left[\frac{1}{50} \ln 0.5 + 0.005\right]$$

$$k = \left(\frac{1}{50}\right)(-0.69) + (0.005)$$

$$k = 0.0086$$

3. Solution

a. By Eq. (4) $D_d = C_o\,(1 - e^{-kt})$

$$C_o = 2 \text{ ppm}$$

$$k = 0.0086$$

$$t = 120 \text{ min}$$

$$kt = 1.03$$

$$D_d = (2)\left[1 - e^{-1.03}\right] = (2)(0.65) = 1.3 \text{ ppm}$$

$$D_s = 0.442 \text{ ppm} \quad \text{ref. solution (1)}$$

$$\frac{D_d D_s}{C_o} = \frac{(1.3)(0.442)}{2.0} = 0.287$$

By Eq. (5) $C_t = C_o - D_d - D_s + \dfrac{D_d D_s}{C_o}$

$$C_{120\text{ min}} = (2.0) - (1.3) - (0.442) + 0.287$$

$C_{120\text{ min}} = 0.543$ ppm of gas A with both decay and sampling diluting the test system for 120 min.

b. If $D_s = 0$, Eq. (5) is:

$$C_t = C_o - D_d$$

$$C_{120} = (2) - (1.3) = 0.7 \text{ ppm}$$

III Example of Corrections Applied in Phase II

A mixture of gases was injected into the 2000-liter tank at t_o, including 1.5 ppm of gas A and 1.5 ppm of gas B. Three samples of gas A and 3 samples of gas B were obtained over a single 120-min period. Each chemical analysis of gas A was obtained by sampling the chamber air through a scrubber for 20 min at 10 liters/min. Each chemical analysis of gas B

was obtained by sampling through a scrubber for 5 min at 8 liters/min. Samples for the analysis of gas A were collected at the following intervals: $t_{0-20\ min}$, $t_{50-70\ min}$, $t_{80-100\ min}$. Samples for the analysis of gas B were collected at the following intervals: $t_{30-35\ min}$, $t_{70-80\ min}$, $t_{115-120\ min}$. An equal volume of fresh air was drawn into the chamber during the sampling periods.

In addition to dilution due to sampling these 2 gases, there was an additional dilution due to continuous sampling for NO_2 at 0.250 liters/min over the entire 120-min period.

As an example, the analysis indicated that there was 1.0 ppm of gas A at $t_{0-20\ min}$, and 1.04 ppm of gas B at $t_{115-120\ min}$. It was then necessary to obtain an approximate correction for dilution due to sampling. The corrections follow.

$$D_S = C_0 \left(1 - e^{\frac{-Qt}{V}}\right) C_0 = 1.5 \text{ ppm} \quad (3)$$

i. (gas A)

$$t_0 = t_{0-20} = 10 \text{ min av. value}$$

$$Q = Q_A + Q_{NO_2} = 10.25$$

$$Qt = 102.5$$

$$\frac{Qt}{V} = 0.05 \quad e^{\frac{-Qt}{V}} = 0.95$$

$$D_{S_{10}} = (1.5)(0.05) = 0.07 \text{ ppm}$$

$$\text{conc.}_{\text{corr.}_{10}} = \text{conc.}_{\text{meas.}_{10}} + D_{S_{10}} = 1.07 \text{ ppm} \quad (4)$$

ii. (gas B) Total gas sampled in 120-min period

$$Qt_{tot} = (Q_A T_A)\, n_A + (Q_{NO_2})(120) + (Q_B T_B)\, n_B$$

where

n_A = number of times gas A was sampled in 120 min

n_B = number of times gas B was sampled in 120 min

t_A = time to draw one sample of gas A

t_B = time to draw one sample of gas B

$$Qt_{tot} = (10)(20)(3) + (0.25)(120) + (8)(5)(3)$$
$$= 600 + 30 + 120 = 750 \text{ liters}$$

Note: $t_{115-120}$ for gas B was not averaged since very little would be gained in accuracy for such a small correction.

$$\frac{Qt_{tot}}{V} = \frac{750}{2000} = 0.375$$

$$D_s = C_0\,(1 - 0.69) = (1.5)(0.31) = 0.46 \text{ ppm}$$

$$\text{conc}_{\text{corr.}_{120}} = 1.04 + 0.46 = 1.5 \text{ ppm}$$

Note: The correction for the concentration of NO_2 at any time t would be made in the same manner as the corrections for gas B were made in ii, above.

IV Example of Corrections Applied in Phase III

The same mixture of gases was injected into the tank at t_0 as was used in Phase II, and 2 gases were sampled intermittently over each 120-min period together with continuous sampling for NO_3 as in Phase II. However, an aerosol was added to the chamber at t_0, and the concentration of the aerosol was monitored continuously over the 120-min period, using a forward scattering photometer. The sampling rate through the photometer was 4.2 liter/min.

Let us consider the same sampling procedure as was described in the preceding section as an example of the treatment of analytical results obtained on Phase III, assuming that the aerosol was added at t_0. It is then necessary to correct the gas concentrations for this additional dilution due to continuous sampling through the photometer, and to correct the photometer reading for all dilution due to sampling.

Total gas sampled in time t is given by:

$$Qt_{tot} = (Q_A t_A)\, n_A + (Q_B t_B)\, n_B + \ldots + (Q_i t_i)\, n_i + Q_{NO_2}\, t + Q_P t \quad ,$$

where P represents the sampling rate through the photometer.

Assume the same experimental arrangement as in Phase II.

t	$(Q_A t_A)(n_A)$	$(Q_B t_B)(n_B)$	$Q_{NO_2} t$	$Q_P t$	Q_{tot}	$e^{-Q_{tot}/V}$	$\left(1 - e^{-Q_{tot}/V}\right)_{tot}$	$D_{s_{A,B}} = C_0\,(1 - e^{-Qt/V})$	
10	100	0	2.5	42	144.5	0.93	0.07	0.10	ppm
35	200	40	8.7	147	395.7	0.82	0.18	0.27	ppm
60	300	40	15.0	252	607	0.74	0.26	0.39	ppm
80	400	80	20	336	836	0.66	0.34	0.51	ppm
90	500	80	22.5	378	980.5	0.61	0.39	0.58	ppm
120	600	120	30	504	1254	0.53	0.47	0.70	ppm

Thus, the corrected gas or particulate concentration at some time x is found by adding the corresponding D_s to the measured value at that time; i.e., $(\text{conc. corr.})_x = (\text{conc. meas.})_x + (D_s)_x$

$D_{s_A} = D_{s_B}$ in the above calculations since $C_{o_A} = C_{o_B} = 1.5$ ppm

D_{s_A} = dilution of gas A due to all sampling.

D_{s_B} = dilution of gas B due to all sampling.

Appendix D

STATISTICAL TREATMENT OF DATA

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STATISTICAL TREATMENT OF DATA

The data were treated statistically in order to discern time trends, confidence intervals for the true slopes of the lines describing the decay of the air pollutants, and day effects on the program, and to estimate the number of samples of each gas which would be required to monitor similar test atmospheres by these sampling and analysis methods in larger chambers. Tests on part I were preliminary, and were made to evaluate sampling and analytical methods which were to be used when monitoring the gas mixture. The presence of day effects was not determined in part I, but time trends and confidence intervals were obtained in order to indicate the effectiveness of the methods in atmospheres containing a single test gas.

Dr. Gerald J. Lieberman, Associate Professor of Statistics at Stanford University, and Dr. Edwin Cox, Statistician at Fort Detrick, suggested the experimental design of parts II and III which is described in the text of this report. This design was used in order to obtain an optimum number of observations of each gas under these experimental conditions, within the time and cost schedules of the project. Due to the length of time required to collect samples, a maximum of six observations could be obtained over a 2-hr period in most cases, and this number was used in designing the experiments.

Part II was considered to be an exploratory phase, in which the gas injection methods were tested, and in which the sampling and analytical methods developed in part I were checked for interferences from the other gases in the complete gas mixture. Two components were run each day, and three samples of each component were collected over the 2-hr period. Samples of the two gases were collected alternately. In order to estimate the variability due to days as well as to experimental error, each component was tested on two days, e.g., a particular gas was sampled at times 1, 3, and 5 on one day, and at times 2, 4, and 6 on the other. The days on which the gases were sampled were chosen at random.

Part III was designed like part II, except that each gas in the gas-aerosol mixture was tested on three days. Nine observations of each gas were therefore obtained, permitting a better measure of experimental error. The particulate material was monitored continuously during each 2-hr test period.

No practical effect of the particulates on the gas mixture was observed, and the data from parts II and III were combined, ignoring the infrequent day effects. The regression lines and experimental error associated with the 15 observations of each gas were then determined.

Finally, an estimate was made of the minimum number of samples of each gas which would be required to monitor similar test atmospheres in other chambers.

A summary of the statistical treatment is given below, using the notation of Bowker and Lieberman (a).

1. Statistical Treatment of Part I; Single Gas in Chamber

The value b_1, the slope of the regression line relating the concentration of a particular gas at a particular time, was obtained by the formula:

$$b_1 = \frac{\sum_{i=1}^{n} (x_i - \bar{x})(y_i - \bar{y})}{\sum_{i=1}^{n} (x_i - \bar{x})^2} \quad (1)$$

The value b_0, the intercept of the regression line, was obtained by the formula:

$$b_0 = \bar{y} - b_1\bar{x} \quad (2)$$

The formula for the regression line was then:

$$y = b_0 + b_1 x \quad (3)$$

The significance of regression line was then determined by first estimating the residual variance around the regression line, using the formula:

$$(n-2)\, s^2_{y/x} = \sum_{i=1}^{n} (y - \bar{y})^2 - \frac{\left[\sum_{i=1}^{n} (x_i - \bar{x})(y_i - \bar{y})\right]^2}{\sum_{i=1}^{n} (x - \bar{x})^2} \quad (4)$$

and then obtaining a value, t, from the formula

$$t = \frac{b_1}{s_{y/x}\sqrt{\dfrac{1}{\sum_{i=1}^{n} (x_i - \bar{x})^2}}} \quad (5)$$

The next step was to determine the confidence interval of the regression slope, using the following formula to represent the interval which includes the true slope at the 95% confidence level:

(a) Bowker, Albert H. and Gerald J. Lieberman. Handbook of Industrial Statistics, Prentice-Hall, Inc., Englewood Cliffs, 1955.

$$\text{true slope} = b_1 \pm \frac{t_{\alpha/2;\, n-2}\, s_{y/x}}{\sqrt{\sum_{i=1}^{n} (x_i - \bar{x})^2}} \tag{6}$$

2. Statistical Treatment of Part II (All Gases in Chamber) and Part III (All Gases and Particulates in Chamber)

The regression lines and the significance of the regression lines were determined in each test consisting of three observations on a particular day, using equations 1 through 5.

The next step was to determine whether or not the regression coefficients for a particular gas obtained on 2 days in part II differed from one another by a significant amount. A value for t was obtained from the formula:

$$t = \frac{b_1^{xy} - b_1^{uv}}{\sqrt{\frac{(n_{xy} - 2)\, s^2_{y/x} + (n_{uv} - 2)\, s^2_{v/u}}{n_{xy} + n_{uv} - 4}}\ \sqrt{\frac{1}{\Sigma(x_i - \bar{x})^2} + \frac{1}{\Sigma(u_i - \bar{u})^2}}} \tag{7}$$

where n = 3, the number of observations on each day. In this test, the regression coefficients were significantly different at the 5% level if $t > 4.303$. A significant difference would indicate the presence of a day effect.

Equation (7) was used in a similar manner to determine day effects in part III, by taking the 3 days in all combinations of 2 days.

If the regression coefficients obtained on different days were not significantly different for a particular gas, the data were combined to obtain a single regression line with slope $\bar{b}$ from equations (1) and (2). The significance of this regression line could then be obtained from equations (4) and (5) where $n - 2 = 4$ degrees of freedom, and $t > 2.776$ in part II, and where $n - 2 = 7$ degrees of freedom, and $t > 2.365$ in part III, if a relationship of time and concentration was present at the 5% significance level.*

The next step was to determine the confidence interval of the regression mean slope, using the following formula to represent the interval which includes the true slope at the 5% confidence level for part II:

* Day effects occurred infrequently, and were ignored in order to obtain information on regression lines and confidence intervals at higher values of n.

$$\text{true slope} = \bar{b} \pm \frac{t\alpha/2;\ n - 4}{2} \sqrt{\frac{s^2_{y/x} + s^2_{v/u}}{2}} \sqrt{\frac{1}{\Sigma(x_i - \bar{x})^2} + \frac{1}{\Sigma(u_i - \bar{u})^2}} \tag{8}$$

and the following formula for part III:

$$\text{true slope} = \bar{b} \pm \frac{t\alpha/2;\ n - 6}{3} \sqrt{\frac{s^2_{y/x} + s^2_{v/u} + s^2_{r/q}}{3}}$$

$$\times \sqrt{\frac{1}{\Sigma(x_i - \bar{x})^2}\ \frac{1}{\Sigma(u_i - \bar{u})^2}\ \frac{1}{\Sigma(q_i - \bar{q})^2}} \tag{9}$$

The data from parts II and III for each gas were then combined, and formulas (1) through (6) were used to determine the regression lines and confidence intervals, where $n - 2 = 13$.

Finally, the confidence limits for the true slopes which were obtained when the parts were combined were considered to be acceptable slope variations when monitoring the gases in future tests under these experimental conditions. An estimate was then made of the number of tests required in order to fall within this variation 95% of the time that the tests would be repeated, using the following formula:

$$d = \frac{/c/}{s_{y/x} \sqrt{\dfrac{n - 1}{\sum_{i=1}^{n} (x_i - \bar{x})^2}}} \tag{10}$$

where $/c/$ is the acceptable variation in the slope. Figure 13.29 of ref. (a) is then entered with d and n in order to obtain an estimate of the number of observations required so that a slope will be obtained which falls within $/c/$ at the 5% confidence level.

The statistical computations were made with an Electrodata 205 (Datatron) located at Stanford Research Institute. The keypunched program is on file in the Institute's Mathematical Sciences Department.

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